

For Higher Secondary Course of West Bengal , also for Plus 2 and Two-year,
Pre-University courses of other Indian Boards and Universities.

AN INTRODUCTION TO CHEMISTRY

VOLUME 1 (PART I)

By

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THIRD EDITION



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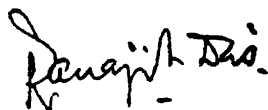
PREFACE TO THE THIRD EDITION

The third edition of the book, 'An Introduction to Chemistry' (Vol I) has just come out. The second edition of this volume was published in July, with minor corrections. However, the reception accorded to that edition has been such that it has given me the opportunity for a further revision within a year.

I hope that the present enlarged and thoroughly revised edition will serve the needs of the students better in understanding the subject and in facing the plus 2 course final examination as well as other competitive examinations with confidence. I am personally indebted to the teachers who sent valuable suggestions for the improvement of the book.

The 15th November

Amt (Howrah)



PREFACE TO THE FIRST EDITION

The wide reception accorded to my 'Higher Secondary Chemistry' in Bengali by the teachers and the taught has encouraged me to write a text book of Chemistry for the Higher Secondary course in English which can cater to the needs of the students prosecuting studies in English medium.

Although the book is primarily written in accordance with the syllabus laid down by the West Bengal Council of Higher Secondary Education, its subject-matter has been so carefully designed and enriched by incorporating additional information that it covers up the syllabi of the Higher Secondary (Plus-2) and Two year Pre University courses of Higher Secondary Boards and Universities of other Indian States.

With the introduction of 10+2+3 pattern, a well-thoughtout syllabus co-ordinating the Secondary and Degree stages has been prescribed by the W B H S Council. In the present H. S. curriculum, there is a marked departure from the traditional treatment of the subject. Moreover, due emphasis has been laid on the modern concepts in order to cope with the rapid development in Chemistry.

In writing the book, I have all along kept in mind the basic idea of the syllabus and have utilised fully my long teaching experience and knowledge gathered from different text books of eminent Indian and foreign authors.

Thorough and systematic treatments of different topics are the salient features of the book. Every concept or principle has been explained in simple and clear language with illustrative examples and explanatory diagrams. Modern theories have also been elaborately dealt with. Details of the preparative and industrial processes, as also the properties of the elements and compounds have been given. No effort has been spared to make the book singularly adequate for students to grasp the different topics to be taught at this level.

I am fully aware of the fact that a proper understanding of the subject of Chemistry requires a thorough grasp of applications of the theoretical concepts and principles through solving a variety of numerical problems. With a view to creating interest amongst the students in this respect, a large number of worked out problems related to each principle have been given. All the steps have been clearly worked out so that the students at this stage understand what they are doing without forming the habit of working out the problems mechanically.

At the end of the book, quite a large number of questions relating to each chapter have been given. Most of them were set in various examinations held by different Indian Boards and Universities or other examining bodies. Each chapter contains broad type, short type and objective type questions framed according to the latest technique.

I confidently hope that the book will help the students in their preparations for various competitive public examinations.

Any criticisms, comments and suggestions for improvement of the book will be gratefully accepted. I shall feel obliged if my attention is drawn to the errors which may have escaped my notice.

The 23rd January,
Amta (Howrah)

Ranajit Das

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ORIGINAL SYLLABUS IN CHEMISTRY

W.B. H.S. COUNCIL

PAPER I (Full Marks – 80)

GROUP A - *General and Physical Chemistry* (Marks – 40)

I. Introduction. Chemistry—an experimental Science. Elements, Compounds and mixtures.

II. Laws of Chemical Combination—Dalton's Atomic Theory critical study. Gay Lussac's Law. Atomic weight (definition).

III. Concept of the Molecule and Avogadro's Hypothesis. Definition of molecular weight. Simple deductions from Avogadro's Hypothesis. Avogadro Number Determination excluded. Mole concept.

IV. Symbols, Formula and Valency. —Chemical equations and their significance. Stoichiometry. Weight to weight, weight to volume and volume to volume calculations. Eudiometry. Vapour density determination omitted, empirical formula and molecular formula.

V. Equivalent weight. Chemical methods of determination of equivalent and atomic weights. Dulong and Petit's Laws. Mitscherlich's Law of isomorphism. Calculations involving atomic and equivalent weights, Parallel calculations using mole concept.

VI. Acidic, Basic, Amphoteric and Neutral Oxides. Hydrides and Oxyacids. Basic Oxides and Hydroxides. Normal, Acid and Basic Salts—Hydrolysis. Equivalent weight of Acids, Base, and Salts. Standard solutions—normal and molar (and formal) solutions. Neutralisation, Indicator. Chemical Calculations on Acidimetry and Alkalimetry.

VII. Oxidation and Reduction—old concept and new electronic concept. Inter-relation between the two. Oxidation number—balancing equations by Oxidation number method (simple examples only from reactions under the purview of the syllabus).

Electropotential series of metals.

VIII. Boyle's Law. Charles' Law, Gas Constant R , $pV = nRT$. Dalton's Law of Partial Pressures. Graham's Law of diffusion of gases.

IX. Law of Mass Action. Dynamic Equilibrium and Equilibrium constant. Le Chatelier Principle and its application to some industrial reactions.

GROUP—B : *Inorganic Chemistry* (Marks—40)

The chemistry of an element or a compound mentioned in this syllabus includes Preparation, Properties, Reaction and uses Laboratory Processes should be included where necessary.

Chemistry of the following.—(Comparative study wherever possible)

I. Oxygen and Hydrogen, Water, Hard water and soft water, Softening of water. Gravimetric and Volumetric Composition of water. Hydrogen peroxide and Ozone

II. Air : Nitrogen

III. The Elements – Carbon, Phosphorus, Sulphur and Halogens (Fluorine excluded.)

CO, CO₂, SiO₂, N₂O, NO, N₂O₃, N₂O₄, N₂O₅, P₄O₆, P₄O₁₀, SO₂, SO₃

IV. *Oxides*

V. *Oxyacids*

Nitrous, Nitric, Phosphorus, Phosphoric, Sulphurous and Sulphuric Acids.

VI. Hydrides—Ammonia, Phosphine, Sulphuretted Hydrogen, Hydrochloric, Hydrobromic and Hydroiodic Acids.

VII. Manufacture (omitting details) of Ammonia (Conversion of Ammonia into Ammonium Sulphate and Urea), Nitric Acid, (Contact process only) and Superphosphate of Lime, Coal Gas.

N.B. In the revised Syllabus for Higher Secondary Examination of West Bengal H S Council for candidates appearing in 1985 and 1986, the following changes have been made. The teachers and students are requested to note the changes

I. The portion parallel calculations using mole concept in the section V will be alternative to any other portion of the original syllabus

II. The numerical problems on (i) Dalton's law of Partial Pressure, (ii) Graham's law of diffusion of gases are not required.

III. Numerical problems on Law of Mass Action are not required.

ATOMIC WEIGHT

Name	Symbol	At.No.	At. wt.	Name	Symbol	At.No.	At. wt.
Actinium	Ac	89	227	Molybdenum	Mo	42	95.95
Aluminium	Al	13	26.98	Neodymium	Nd	60	144.27
Americium	Am	95	243	Neptunium	Np	94	237
Antimony	Sb	51	121.76	Neon	Ne	10	20.183
Argon	A	18	39.44	Nickel	Ni	28	58.71
Arsenic	As	33	74.91	Niobium	Nb	41	92.91
Astatine	At	85	210.	Nitrogen	N	7	14.008
Barium	Ba	56	137.36	Osmium	Os	76	190.2
Berkelium	Bk	97	249	Oxygen	O	8	16.000
Beryllium	Be	4	9.013	Palladium	Pd	46	106.4
Bismuth	Bi	83	209.00	Phosphorus	P	15	30.976
Boron	B	5	10.81	Platinum	Pt	78	195.09
Bromine	Br	35	79.916	Plutonium	Pu	94	242
Cadmium	Cd	48	112.41	Polonium	Po	84	210
Calcium	Ca	20	40.03	Protactinium	K	19	39.100
Californium	Cf	98	248	Praseodymium	Pr	59	140.92
Carbon	C	6	12.011	Promethium	Pm	61	145
Cerium	Ce	58	140.13	Protoactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.22
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium, see Niobium				Rubidium	Rb	37	85.48
Copper	Cu	29	63.54	Ruthenium	Ru	44	101.1
Curium	Cm	96	245	Samarium	Sm	62	150.35
Dysprosium	Dy	66	162.51	Scandium	Sc	21	44.96
Erbium	Er	68	167.27	Selenium	Se	34	78.96
Europium	Eu	63	152.0	Silicon	Si	14	28.09
Fluorine	F	9	19.00	Silver	Ag	47	107.880
Francium	Fr	87	223	Sodium	Na	11	22.991
Gadolinium	Gd	64	157.26	Strontium	Sr	38	87.63
Gallium	Ga	31	69.72	Sulphur	S	16	32.066
Germanium	Ge	32	72.60	Tantalum	Ta	73	180.95
Gold	Au	79	197.0	Technetium	Tc	43	99
Hafnium	Hf	72	178.50	Tellurium	Te	52	127.61
Helium	He	2	4.003	Terbium	Tb	65	158.93
Holmium	Ho	67	164.94	Thallium	Tl	81	204.39
Hydrogen	H	1	1.008	Thorium	Th	90	232.05
Indium	In	49	114.82	Thulium	Tm	69	168.94
Iodine	I	53	126.91	Tin	Sn	50	118.70
Iridium	Ir	77	192.2	Titanium	Ti	22	47.90
Iron	Fe	26	55.86	Tungsten	W	74	183.86
Krypton	Kr	36	83.90	Uranium	U	92	238.07
Lanthanum	La	57	138.92	Vanadium	V	23	50.95
Lead	Pb	82	207.21	Wolfram, see Tungsten			
Lithium	Li	3	6.940	Xenon	Xe	54	131.30
Lutetium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.94	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.23

SOME USEFUL MEMORANDA

Weight of 1 c.c. of hydrogen at N.T.P. = 0.000089 gm.
 = 0.00009 gm

Normal or standard temperature = 0°C or 273°A

Normal or standard pressure = Pressure of a column of
 mercury 76 cm high.

Volume of 1 gm-molecule of a gas at N.T.P. = 22.4 litres

Molar gas constant (R) = 0.082 litre atmosphere per
 degree absolute per mole.

Avogadro's number (N) = 6.023×10^{23}

1 Faraday = 96,500 coulombs.

GROUP A
GENERAL AND PHYSICAL CHEMISTRY

INTRODUCTION

A perfect and systematic knowledge of different subjects of nature is collectively known as science or *natural science*. Nowadays, the word science is generally used to describe man's orderly search for knowledge by methods of careful observations and controlled experiments. For convenience of study, natural science has been divided into different branches. Chemistry is one of the most important and highly developed branches of science. According to the belief of the Western scholars, the term chemistry has been derived from Egypt's ancient name *Chemia* which signified a divine art, much developed and widely practised in that country during the first few centuries of the Christian era.

The material world around us consists of an infinite variety of substances, each of which has its own shape, size, colour and specific properties. Water, air, soil, gold, iron, common salt etc. are different varieties of substances, but in no case two of them exhibit the same properties.

In the living bodies as well as in the non-living substances, innumerable changes are going on either spontaneously or when acted upon by physical forces like pressure, heat, electricity etc., or by other substances or by both acting together. Kerosene or petroleum when burnt emits light and gradually disappears. A piece of coal on ignition produces heat and is ultimately converted into a small amount of ash. The various types of food we take suffer numerous changes within our bodies before they are absorbed in the blood stream. In fact, we maintain our growth and nourishment and derive strength for all of our activities due to assimilation of food materials. Guided by natural instinct and intelligence, man makes attempts to know how and why these changes are occurring and to identify the new substances formed as a result of such changes.

As a matter of fact, from time immemorial man has been trying to break or analyse the substances around him and to prepare them from other substances with the help of meagre means at his disposal. In course of time he has been able to discover certain natural laws governing the formation and changes of matter.

The success achieved by man in his century long search for knowledge about the matter and its transformation has given the science of chemistry its modern developed shape.

Chemistry is that branch of science which deals with the composition, characteristic properties, methods of preparation of substances and the various changes they undergo in their compositions spontaneously or by application of external physical forces or when treated with other substances under diverse conditions. The science of chemistry is also concerned with the gain or loss of energy accompanying such changes and the laws and theories governing these changes.

Branches of Chemistry :

Both from the theoretical and practical points of view, the field of chemistry has grown so vast in recent years that it has become quite impossible to comprehend the subject in one treatise. So, for convenience of study, chemistry has now been divided chiefly into three branches, such as (a) Inorganic chemistry, (b) Organic chemistry and (c) Physical chemistry.

Inorganic chemistry is that branch of chemistry which is mainly concerned with the study of the minerals. It deals with the study of the elements in general and the compounds formed by the mutual combination of the elements (except carbon and its compounds).

Organic chemistry : Due to certain peculiar characteristics, the element carbon can form enormous number of compounds which are of vital importance in the biological world. The study of carbon and its compounds has developed a distinct branch of chemistry known as *Organic chemistry*. The name has been derived from the fact that the carbon compounds dealt with under this branch are generally allied to the products of organs of animals and plants.

This definition includes several simple compounds of carbon, such as carbon dioxide, carbon monoxide, carbonates, carbon disulphide etc., which are obtained from inorganic sources. These compounds are usually studied under inorganic chemistry.

Physical chemistry is concerned with the elucidation and classification of theoretical principles of the subject. It mainly deals with the fundamental laws that govern transformation of matter. The effects of temperature, pressure, electricity, light, concentration etc., on reacting substances come under the scope of physical chemistry.

To cope with the extraordinary progress of the subject of chemistry, it has further been subdivided into other branches, some of which are stated below.

Analytical chemistry is now a days taken as a special branch of chemistry which deals with the various techniques and procedures adopted in the identification and estimation of the constituents of the chemical substances.

Biochemistry is the chemistry of living organisms. This branch of chemistry aims at investigating the nature of substances produced in the living bodies and seeks to account for or explain the chemical

reactions taking place in such production. The effect of foreign substances on the living bodies and the reactions in presence of micro organisms are also studied under this head. In the light of new discoveries and improved techniques, *the medicinal or pharmaceutical chemistry* has now been given the rank of a special branch of chemistry which deals with the use of chemicals to prevent and cure diseases in living beings.

Applied Chemistry : In the modern age, chemistry plays an important role in industry. It is justified to say that the progress of a country is symbolised by the progress of its chemical industries. Thus applied chemistry is a special branch of chemistry which is concerned with the chemistry and techniques of the industrial processes. In view of its importance in the production of chemicals of everyday use as also the chemicals that meet the needs of ever advancing human civilisation, this branch has ultimately grown to be a full fledged subject matter of learning.

Soil (or Agricultural) Chemistry deals with the chemical studies of the soil and the use of suitable chemical substances to increase its fertility. It also deals with the chemicals used to destroy the insects or other organisms which are regarded as the enemies of the plants. It is a very important branch of chemistry as it aims at growing more agricultural products for solving the food problems confronted by almost all countries of the world due to ever increasing rate of population.

Nuclear (Radio) Chemistry It is the youngest of the branches of chemistry so far discussed. It is concerned with the study of the radio active elements, isotopes and their various applications. The artificial transmutation of elements also falls under the purview of this branch.

Chemistry --an Experimental Science :

Experiments play a very vital role in the study of chemistry in the present days. Modern chemists firmly believe that knowledge in chemistry can never be perfect unless its truths are experimentally verified. This is why they are inclined more and more to take recourse to experimentations and inferences derived from them by careful reasonings.

It cannot be denied that imagination and speculations contributed a lot in the early development of the subject. But to a modern chemist ideas based on mere intuitions are of very little values.

Chemistry, as stated earlier, is a science which deals with the matter and its transformations under varying conditions.

A good chemist devises methods which cause regulated changes to occur in matter and draws inferences by observing the controlled sequence of changes.

The experiments not only help us in characterisation and identifica-

tion of a substance but also predict the changes that an unknown substance should undergo.

It has been proved that the use of a chemical substance for a particular purpose is solely dependent on its composition or constitution which can only be known by collecting analytical and synthetic evidences based on different experiments on the substance.

We may conclude that chemistry is no longer a science which deals with the changes of matter only. But it is primarily concerned with the development of clear understanding of *how* and *why* the changes are taking place.

Changes of matter—Physical and Chemical changes. The changes that matter undergoes fall into two distinct classes, namely physical and chemical. Any change which does not alter the composition (or internal constitution) of a substance is referred to as a *physical change*. Obviously in a physical change, a substance is never converted into another substance and the weight of the original substance remains unchanged. It only causes to alter a few of the minor physical characters of the substance. A physical change is temporary in nature and the substance regains its original form upon withdrawing the agency which brings about the change.

When water is heated at its boiling point, it entirely escapes in the form of steam. Again, when electric current is passed through acidulated water, it is converted into gases and gradually disappears. The changes water suffers in these two cases do not belong to the same category. The first one is a physical change and the second is a chemical change. The change taking place in the conversion of water to steam does not disturb the composition (or internal constitution) of water. It simply affects some physical properties of water—such as state of aggregation, density, appearance etc. On cooling steam is turned back to same weight of water as before and both water and steam possess the same chemical properties.

On the other hand, electric current causes water to decompose into two gases, hydrogen and oxygen. The properties of these gases are entirely different from those of water. Moreover, the gases can never be reconverted into water by cooling only. So, the change that water suffers during the passage of electric current is a chemical change. Here, one substance has been changed permanently into two new substances with an altogether new set of properties.

A piece of platinum wire when held in the nonluminous flame of a Bunsen burner becomes red hot first and then white hot emitting light. But on removing the wire from the flame, it is restored to its original condition and has the same weight as before. Thus a platinum wire suffers a physical change while it is being heated in a flame. But if a piece of copper wire is heated in the flame, it burns for some time with a bluish flame and finally the colour of the flame disappears. On cooling, the wire assumes a black colour. In fact, the

metallic copper on being reacted with oxygen of the air at a high temperature is converted into a new substance—cupric oxide. This is certainly an example of a chemical change.

It must be kept in mind that in a physical change, a thermal change may or may not occur. But the exchange of heat is one of the main criteria of the chemical change. A chemical reaction is always attended with evolution or absorption of heat.

Classification of matter—Elements and Compounds :

Most of the innumerable substances around us are pure. From the standpoint of chemistry, a pure substance is defined to be a substance which is made up of one kind of material only. The resulting substance produced by mixing more than one pure substance is not regarded as a pure substance.

Any pure substance is homogeneous. A substance is said to be *homogeneous* when each and every part of it exhibits the same properties and has the same composition. A homogeneous substance has definite properties and uniform composition throughout. Examples are, pure sugar, water, common salt etc.

Impure substances generally appear to be heterogeneous. A substance is referred to as *heterogeneous* when different parts of it possess different properties and composition. A heterogeneous substance is made up of two or more varieties of matter. A mixture of sugar and sand in any proportions by weight is an example of a heterogeneous substance. But it is to be remembered that homogeneity is not the only criterion to decide whether a substance is pure or not. The solution obtained by dissolving sugar in water is homogeneous as it has the same composition and properties in all its parts.

Although milk is a substance having a number of constituents, it is homogeneous. But the sugar solution or milk can in no way be taken as a pure substance. On the basis of internal constitution, the pure substances have been divided into two classes, namely elements and compounds.

✓ **Element :** An element is a simple homogeneous substance which cannot be resolved or split up into any simpler and dissimilar substances as a result of ordinary chemical analysis. In other words, a simple substance which cannot be chemically decomposed to any substance other than itself is an element.

Thus oxygen is an element because it is not analysable to other substance or substances with different properties. Hydrogen, nitrogen, sulphur, carbon, sodium, iron, gold etc., are familiar examples of elements.

Elements existing in solid, liquid and gaseous states are known. There are 92 common elements which are found to occur in nature. However, at present the scientists have discovered some more elements beyond uranium. They are not naturally occurring elements and are prepared artificially. These elements are called *transuramic elements*.

Based on some of the physical and chemical properties, the elements have been divided into two groups. (a) metals and (b) non-metals. Gold, iron, sodium, calcium etc., are metals. Metals are generally good conductors of heat and electricity. Metals possess a shining appearance called metallic lustre and are generally solid substances with high specific gravity. Some exceptions are also known. Mercury, although a metal, is a liquid at ordinary temperature. Sodium and potassium are definitely metals but are lighter than water. Moreover, metals are found to possess certain characteristic properties like ductility, malleability etc. In general, metals are electropositive elements with high melting points.

On the other hand, hydrogen, nitrogen, carbon, sulphur, phosphorus etc., are non-metals. Non-metals are generally bad conductors of heat and electricity. There are exceptions in this regard. Graphite, a non-metal, is a good conductor of heat. Non-metals do not possess any lustre of their own (non-metals like iodine and graphite possess metallic lustre). Non-metals are generally solids and gases at ordinary temperature. (bromine, a non-metal, is a liquid at ordinary temperature.) In general, solid non-metals have low specific gravity and low melting points (solid boron, carbon being definitely non-metallic elements have high melting points). The properties like malleability, ductility etc., are absent in non-metals. The properties discussed here are not all in characterising these two types of elements. Some more in this respect will be described later.

There are some elements with intermediate properties i.e. they exhibit more or less properties of both metals and non-metals. These elements are referred to as metalloids. Examples are arsenic, antimony etc.

✓ **Compound:** *A compound is a homogeneous pure substance which can be decomposed by chemical methods into two or more simpler substances with different properties. In other words, the substance which is produced by the chemical union of two or more elements in definite proportions by weight is a compound. It has fixed and specific properties altogether different from those of the elements of which it is constituted. A compound can be split up into its ingredients by application of chemical methods.*

Water is a compound. When electric current is passed through water slightly acidified with dil. sulphuric acid, it decomposes into the elementary gases—hydrogen and oxygen. It has been found that the properties of water are entirely different from those of either hydrogen or oxygen. On the other hand, water is produced if electric spark is made in a mixture of hydrogen and oxygen present in requisite proportions. Results of chemical analysis show that in all samples of pure water, 1 part by weight of hydrogen combines with 8 parts by weight of oxygen. Sugar, common salt, chalk, carbon dioxide are well-known examples of compounds.

Mixture or mechanical mixture : A mixture, also called a mechanical mixture, is the resulting substance produced by mere mixing of two or more substances (elements or compounds or both) in any proportions by weight so that the different components simply remain side by side without undergoing any chemical union between them. The components in a mixture retain their respective properties or individual identities and can be separated from one another by easy mechanical processes. Thus, air is a mixture of mainly two gases—nitrogen and oxygen. Of course, it contains some other gases in minute amounts. Gunpowder is a mixture of three solid substances—sulphur, carbon and nitre. The solution which is obtained by mixing sugar or common salt with water is nothing but a mixture of a liquid and a solid substance. Aerated waters are mixtures as these are mainly solutions of carbon dioxide in water under pressure. As soon as the pressure is released gaseous carbon dioxide is found to escape producing bubbles.

B The different substances which form a mixture are called its components as they are lying side by side without change and are separable from each other without change.

Distinction between a mechanical mixture and a chemical compound.

Mechanical mixture	Chemical compound
<p>1 The components in a mechanical mixture may be present in <i>variable proportions by weight</i>. Iron filings and powdered sulphur may be mixed in any proportions by weight to produce a mechanical mixture of the two elements.</p> <p>2 In a mechanical mixture, individual properties of the components remain unaltered. No substance with new properties is formed, i.e. the components are found lying side by side.</p> <p>If a magnet is held near a mixture of iron and sulphur powder, iron particles are attracted by the magnet or when dilute sulphuric acid is added to the mixture iron will dissolve in the dil. acid producing a odourless, inflammable gas named hydrogen. Again, if the mixture is shaken with liquid carbon disulphide, sulphur dissolves leaving iron powder unattacked. Thus in the mixture under reference, the properties of both iron and sulphur are retained.</p>	<p>1 The constituents in a chemical compound must always be present in <i>definite and fixed proportions by weight</i>. Fixed composition is the most important criterion of a compound. In ferrous sulphide, a compound of iron and sulphur, 7 parts by weight of iron are found in combination with 4 parts by weight of sulphur. No sample of ferrous sulphide is known where this weight ratio is not maintained.</p> <p>2 In a chemical compound, the properties of its constituents are completely changed. The compound formed possesses properties which are specific to itself and entirely different from those of its constituents.</p> <p>Ferrous sulphide, a compound of iron and sulphur, is not attracted by a magnet. When treated with carbon disulphide, no constituent is found to dissolve in it. On adding dil. sulphuric acid to ferrous sulphide, a new gas named sulphuretted hydrogen possessing an offensive smell is evolved.</p> <p>This shows that ferrous sulphide is quite different from its constituents (iron and sulphur) in properties.</p>

<i>Mechanical mixture</i>	<i>Chemical compound</i>
<p>3 The components of a mechanical mixture can be separated from one another by easy mechanical means</p>	<p>3 A compound may be separated into its constituent elements only by chemical means and not by any mechanical method</p>
<p>From a mixture of iron filings and sulphur powder iron may be separated by drawing a magnet over it and sulphur by extraction with carbon disulphide</p>	<p>Iron or sulphur present in ferrous sulphide cannot be separated by the mechanical processes. They can however be separated with difficulty using different chemical reactions</p>
<p>4 There is usually no thermal change during the preparation of a mixture. In case of making a few solutions some heat changes are observed. No heat is evolved or absorbed when iron and sulphur powder are simply mixed to form a mixture</p>	<p>4 There is always a thermal change (heat is either evolved or absorbed) during the formation of a compound</p> <p>Formation of ferrous sulphide from iron and sulphur is attended with evolution of much heat</p>
<p>5 A mechanical mixture is usually heterogeneous in character but homogeneous in cases of solutions or mixtures of gases. When a mixture of iron and sulphur powder is seen through a magnifying glass or a microscope separate particles of iron and sulphur are found to exist and remain side by side</p>	<p>5 A chemical compound without any exception is always homogeneous in character</p> <p>In ferrous sulphide the ingredients are not separately recognisable even under a very powerful microscope</p>
<p>6 A mechanical mixture has no fixed melting point or boiling point. It varies according to the ratio of its constituents</p>	<p>6 A chemical compound is generally characterised by a sharp and constant melting point (if solid) and a constant boiling point (if liquid)</p>

4/ It has already been pointed out that there will be inevitably a heat change during the formation of a compound from its elements. In fact a chemical reaction will take place with either evolution or absorption of heat

A chemical reaction which is attended with evolution of heat is known as *exothermic* and the substance formed by such a reaction is called an *exothermic compound*. During the formation of carbon dioxide by burning 12 gms of carbon in 32 gms of oxygen 9400 cal of heat are evolved. 28 gms of nitrogen and 6 gms of hydrogen unite chemically to produce ammonia with evolution of 2200 cal of heat. So carbon dioxide and ammonia are exothermic compounds.

On the other hand a reaction which takes place with absorption of heat is called an *endothermic reaction* and when a substance is formed with the absorption of heat it is said to be an *endothermic compound*. It has been found that heat is absorbed during the formation of ozone from oxygen, carbon disulphide from carbon and sulphur, nitric oxide from nitrogen and oxygen. So carbon disulphide, nitric oxide etc. are examples of endothermic compounds.

Separation of components of a mixture: Separation of components of a mixture in the pure form is done with the help of some common laboratory processes such as filtration, distillation, sublimation, crystallisation etc.

Here the separation involving filtration, sublimation, distillation and solvent extraction has been described. The process of crystallisation

sation and its application have been explained in chapter IV, Group A, Vol. II of this book.

✓(1) **Filtration :** *The process of separating a liquid from one more insoluble solids present in it with the help of a porous material, is known as filtration.*

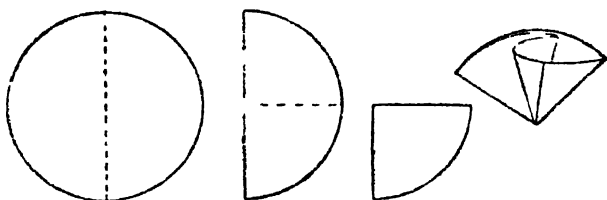
The process consists of pouring the mixture of the liquid and the insoluble substance or substances into some porous material such as, filter paper, glass wool, asbestos fibres, fine cloth, etc. which allow the liquid (a pure sample or a solution containing dissolved substances) to pass through but arrests the undissolved solid matter. In the laboratory, the porous material commonly used is the filter paper.

The clear liquid passing through the porous medium is called the filtrate and the insoluble or suspended matter which is retained, is called the residue.

The process of filtration may be illustrated by separating the ingredients of a mixture of sand and common salt (NaCl).

Common salt is completely soluble in water while sand is insoluble in this solvent. So, when sufficient quantity of water is added to the mixture and stirred common salt goes into the solution and sand does not. The solution of common salt is then separated from sand by filtration.

In the laboratory, a sheet of circular filter paper is folded into two halves along a diameter and then again into two more halves symmetrically along the radius perpendicular to the diameter. Thus, four

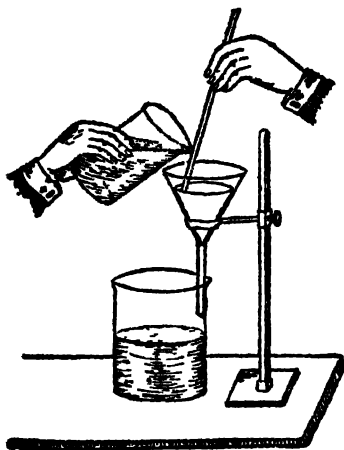


Folding of filter paper

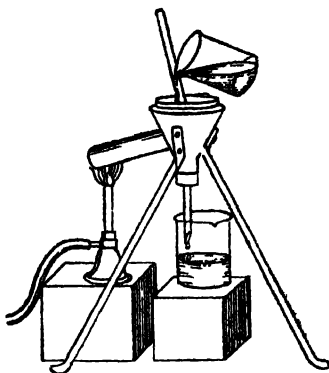
folos in a quadrant are obtained. It is then opened with three folds on one side and one on the other so that a cone is formed. This is fitted in a glass funnel by pressing with the fingers and is fixed smoothly to the funnel by moistening it with a few drops of water. The funnel with the filter paper is placed on the ring clamped to a stand. An empty clean beaker, is kept under the funnel in such a position that the stem of the funnel touches the inner side of the beaker. Now, the beaker containing the salt solution and undissolved sand is held in a slightly inclined position and the mixture is poured slowly on the thicker side of the filter cone down a glass rod. The clear salt solution passes through the filter paper, runs through the stem of the funnel, collects in the beaker below while the insoluble sand being too large to pass through the pores is held on the filter paper.

Sand on the filter paper is taken in a basin and dried by heating.

The filtrate (i.e., solution of common salt in water) is taken in a large evaporating porcelain basin. The basin is heated when water is driven out in the form of steam and the solid common salt is recovered from its solution.



Filtration

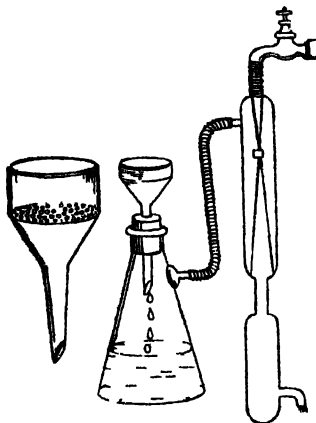


Hot filtration

Hot filtration: Sometimes it becomes necessary to carry out the process of filtration in a hot condition. In such a case the funnel with the filter paper is placed in a double-walled copper funnel filled with hot water and provided with a slanting cylinder closed at the bottom which is slowly heated by a Bunsen burner.

Rapid filtration or filtration under reduced pressure:

For quick filtration in the laboratory the process is carried out under reduced pressure. In this process a special type of porcelain funnel with a perforated disc inside (usually a Buchner funnel) is fitted by means of a rubber cork to a filtering flask in which a partial vacuum is created by connecting its side tube with a water suction pump. A filter paper of proper size is placed on the perforated disc and the liquid to be filtered is poured on the funnel. The liquid passes rapidly through the filter paper into the flask.

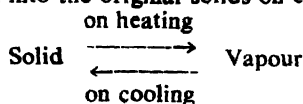


Filtration under reduced pressure

under the influence of the atmospheric pressure. The residue is left on the filter paper.

✓ (2) **Sublimation** : It is generally observed that when a solid is heated, it first melts into a liquid which on further heating vaporises at its boiling point. The vapour, on the other hand, when cooled first condenses into a liquid which then solidifies on further cooling.

But there are certain solids such as ammonium chloride, iodine, camphor, naphthalene etc. which when heated pass directly into the vapour state without passing through the intermediate liquid state and the vapours pass back into the original solids on cooling,



✓ Such solids are said to sublime.

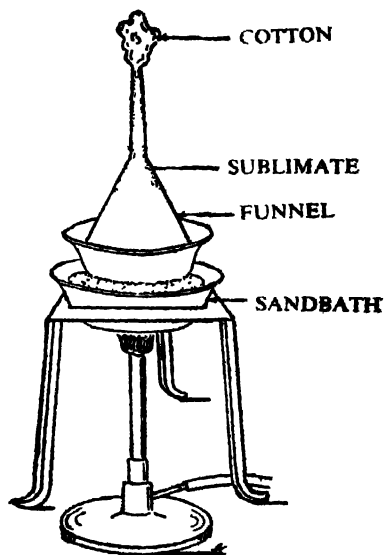
The process of direct conversion of a solid substance into its vapour (without being converted to the liquid state) by application of heat and reversion of the vapour quickly into the same solid on subsequent cooling is known as sublimation.

✓ The solid obtained as a result of condensation of the vapour is called the *sublimate*.

The sublimate has the same chemical composition as the original solid. If a mixture contains a volatile solid that sublimes, the process of sublimation can be easily employed for its separation in the pure state from the other non volatile solid components like sand, sodium chloride etc. of the mixture.

To separate a mixture of ammonium chloride and salt :

We know that ammonium chloride sublimes when heated but common salt does not. So, the components of the mixture can be separated from each other by sublimation. Usual method involving filtration can not applied in this case as both of the salts are soluble in water. The given mixture of the two solids is taken in a porcelain basin which is placed on a sand bath supported on a tripod stand. The mixture in the basin is then covered completely with a inverted funnel having a long stem the opening of which is plugged with a piece of cotton. The outer surface and the stem of the funnel are wrapped with a piece

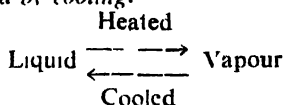


Sublimation

the funnel are wrapped with a piece

of thin cloth or filter paper soaked in water. Now, the basin with its content is heated mildly on the sand bath with a Bunsen burner. Ammonium chloride first vaporises and then deposits as a solid on the cooled inner surfaces of the funnel. When no further sublimate collects, the Bunsen flame is removed, basin is taken out of the sand bath and is allowed to cool. The sublimate of ammonium chloride is next collected on a filter paper by scraping the inner wall of the funnel. The non volatile sodium chloride is left behind in the basin.

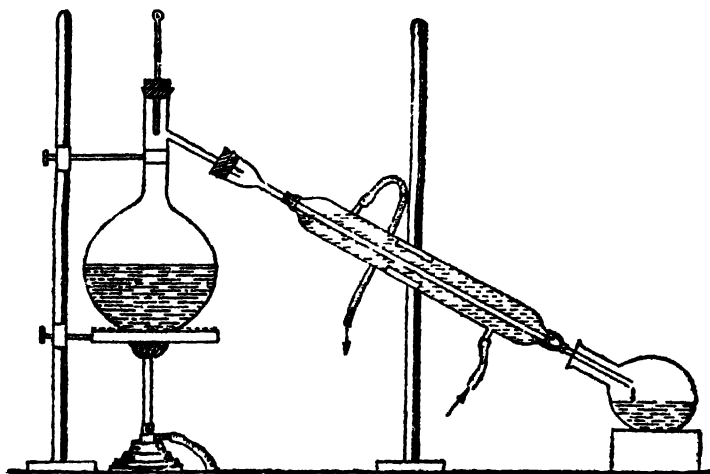
(3) **Distillation :** *Distillation is the process of converting a liquid into its vapour by the application of heat and then condensing the vapour back to the same liquid by cooling.*



Obviously, distillation is a combination of two processes i.e. vaporisation and condensation.

Distillation = Vaporisation + Condensation

The liquid received back by the condensation of the vapour is called the *distillate*. The distillation is employed in the separation of a liquid in the pure state from the non volatile solid or solids either in solution or in suspension. Both the liquid solvent and the solid solute can be recovered by this process.



Distillation

Generally, a distilling flask having a side tube is half filled with the liquid (say an aqueous solution of common salt) and is set up on a

wire gauze on a ring fixed to a stand. The flask is then clamped in position. The mouth of the flask is closed by a cork through which a thermometer is inserted with its mercury bulb standing just below the opening of the side tube.

The side tube of the flask is connected by a bored cork with a Liebig's condenser kept in an inclined position with the help of a clamp and a stand. The lower end of the condenser is introduced into a clean flask which serves as the receiver of the distillate. The Liebig's condenser consists of a narrow glass tube surrounded by a wider jacket tube having two small lateral tubes. The inlet or the lower side tube of the condenser is connected with a water tap by means of a rubber tubing while the rubber tube attached to the outlet or the upper side tube is led into the sink. Thus, a stream of cold water is passed constantly through the jacket tube. The liquid in the distilling flask is slowly heated to boiling when the temperature of the liquid remains constant. The vapour steam in the case of aqueous solution of common salt produced enters the condenser. While passing through the cold inner tube of the condenser, it condenses back to the original liquid and collects in the receiver drop by drop. To avoid bumping of the boiling liquid, a few pieces of glass beads may be added to it. The liquid so collected is free from any dissolved solid. The non-volatile solid (or solids) which was originally present in the liquid before distillation remains in the flask.

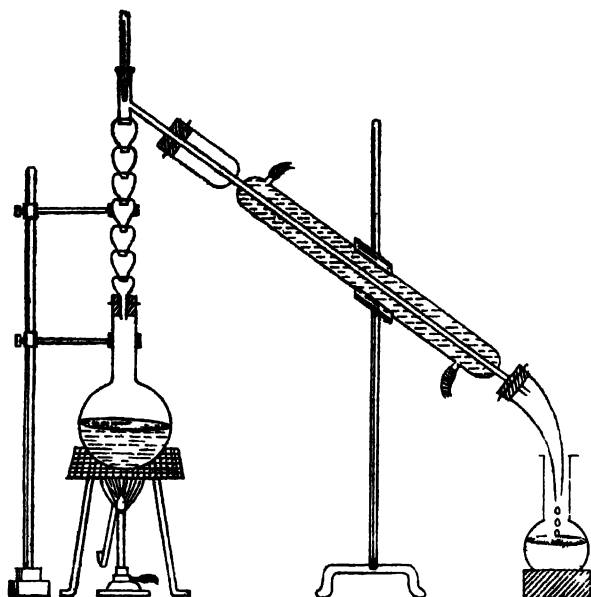
Fractional distillation *The process of distillation which is used to separate the components of a mixture of mutually miscible liquids with boiling points fairly apart is known as fractional distillation.*

The mixture of liquids whose boiling points are widely different is placed in the distilling flask and is heated. The liquid with the lower boiling point distils over first and is collected as the distillate. When nearly whole of it has passed over, the temperature of the remaining liquid begins to rise and reaches the boiling point of another liquid which then begins to distil over. It is now collected in a separate receiver. Thus by collecting the distillate by fractions, two or more volatile miscible liquids can be separated from each other more or less completely.

Fractionation of a mixture of miscible liquids can be more effectively carried out by inserting a *fractionating column* between the distilling flask and the Liebig's condenser as shown in the next figure. The fractionating column provides a large cooling surface to the hot vapours so that the vapours of the higher boiling liquid get condensed and return to the flask while the vapours of the liquid of lower boiling point pass over and condense to liquid in the condenser.

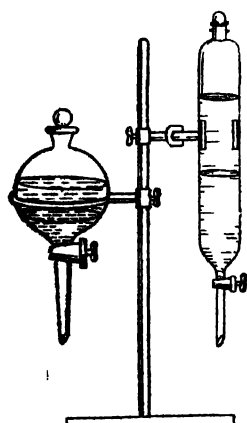
Distillation under reduced pressure Liquids which are susceptible to decomposition at their boiling points can not be distilled under the atmospheric pressure. If the pressure on the surface of the liquid is reduced to create a partial vacuum inside the distilling flask by connecting it with a suction pump through the condenser and

the receiver, the liquid distils at a temperature below normal



Fractional distillation

boiling point The process of distillation under reduced pressure has been fully described in Chapter I Group B of this book under the concentration of hydrogen peroxide



Solvent extraction

Ether is added to an aqueous solution of iodine placed in a

(4) **Solvent extraction:** It is a process which can be effectively used to separate the ingredients of the mixture of various types such as the mixtures containing different solids or different liquids or solid and liquid. The principle of solvent-extraction is based on the preferential solubility of one of the components of the mixture in a particular solvent usually a low boiling organic solvent which forms a distinctly separate layer with the other liquid if present in the mixture.

The method is illustrated here by the extraction of iodine from its solution in water by means of ether or carbon disulphide.

separating funnel. The funnel is then stoppered and shaken gently at first and then more vigorously, the stopper being opened from time to time to allow the excess of ether vapour to escape. Most of iodine passes into the upper layer of ether which is coloured dark brown due to the dissolution of iodine. The lower aqueous layer is run off and the ethereal layer is poured out. When ether is removed cautiously by distillation over water bath, iodine is obtained.

Instead of ether, carbon disulphide may be used to extract iodine, the solution in this case assumes a violet colour and forms the bottom layer in the separating funnel, as carbon disulphide is heavier than water.

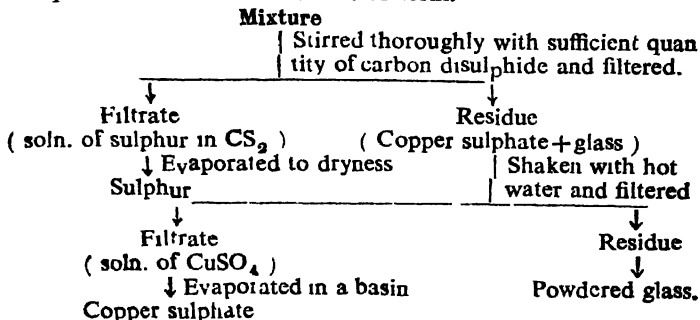
More examples of separation of mixtures :

(A) Separation of a mixture of powdered glass, sulphur and copper sulphate :

The separation of the components of the mixture is based on the following facts.

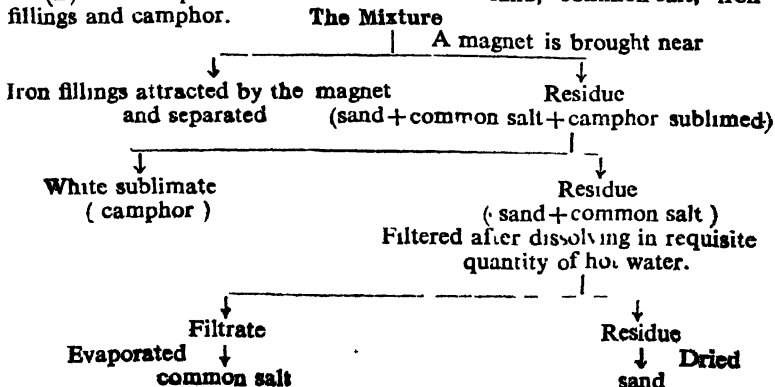
- (i) Sulphur is soluble in carbon disulphide.
- (ii) Copper sulphate is soluble in water but insoluble in CS_2 .
- (iii) Powdered glass is insoluble in carbon disulphide as well as in water.

The separation is shown in the tabular form.



The components of gun powder which is a mixture of sulphur, nitre and charcoal can be separated similarly.

(B) The separation of a mixture of sand, common salt, iron filings and camphor.



CHAPTER 2

LAWS OF CHEMICAL COMBINATION : DALTON'S ATOMIC THEORY

✓ The terms *fact*, *law*, *hypothesis* and *theory* are frequently used in the discussion of various scientific topics. So, the beginners should clearly know the meaning of the terms and the distinction between them.

Fact : (Facts are those which without any exception proceed or happen in a definite manner.) Thus, water is always converted into ice when subjected to cooling and is vapourised on heating. A piece of coal moistened with kerosene or petrol burns more easily and brightly in air than a piece of ordinary coal. A fruit from a tree falls on the ground. The same has never been observed to go upwards when detached from a tree. All these instances described here are familiar examples of facts. Facts can be perceived by our senses and can be verified by actual experiments. In fact, the aim of science is to explain facts correctly and logically.

✓ **Law :** By performing a series of experiments on similar facts and observing the results, the scientists arrive at certain general conclusions which form the basis of a scientific law.

The law in science is a generalisation of closely related facts in a simple and short statement. It is based on well thought experiments and careful observations. (In short, a law is the shortest description of experimentally verified facts.) Sometimes, a mathematical expression is used for a law.

It is an observed fact that at constant temperature, the volume of a given mass of any gas independent of its nature diminishes in a regular fashion with rise of pressure and increases when the pressure is decreased. The general statement on this fact is known as Boyle's law. The observation on the fact that a fruit detached from a tree falls on the ground led to the formulation of one of the most important and fundamental laws of natural science i.e., law of gravitation.

The law is true or valid so long as no fact in conflict with it is known and when such conflicting facts come to light, the law has to be amended or even discarded.

✓ **Hypothesis :** (*The speculation or assumption on the basis of which observed facts or natural laws are explained and correlated is called a hypothesis.*) Obviously, the term is based on imagination and not on experimental facts. A hypothesis, though of speculative origin, is found to contribute much towards the development of science. It is not only able to explain facts already known but predicts new facts of related nature.

Theory : (When the predictions followed from a hypothesis can stand the tests of experiments, the hypothesis attains the status of a *theory*. Both hypothesis and theory are speculative terms.) A theory must prove itself useful in the correlation or interpretation of known facts and prediction of new ones, the truth of which is to be experimentally established.

When a theory fails to cope with the newly discovered facts or the theory makes predictions which when subjected to experimental verification are found to be incorrect, the theory is either modified or abandoned in favour of another.

It is to be noted that a law in science is a generalisation of observed facts only but a hypothesis is a term based on speculation which even goes beyond observed facts.

(✓) **The Laws of chemical combination :** There are altogether five simple but fundamental laws which govern the combination of elements to form compounds and the chemical reactions in general. The laws are —

(1) **The Law of Conservation of Mass or Law of Indestructibility of Matter** (Lavoisier, 1774)

(2) **The Law of Definite or Constant Proportions** (Proust, 1799)

(3) **The Law of Multiple Proportions** (Dalton, 1803)

(4) **The law of Reciprocal Proportions or the Law of Combining Weights** (Richter, 1799)

(✓) (5) **The Law of Gaseous Volumes** Gay Lussac, 1808)

The first four laws are related to the weights of the combining elements and are known as laws of stoichiometry. The last one deals with the combination of gases by volumes. ✓

The Law of Conservation of Mass or Law of Indestructibility of Matter : It is one of the most fundamental laws of natural science and forms the basis of all quantitative works in chemistry. In nature, matter is undergoing innumerable changes but the total mass does not suffer any loss or gain due to these changes. Lavoisier established the truth by performing a series of experiments and enunciated a law which states

(In a chemical change, the sum of the masses of the reacting substances (reactants) is equal to the sum of the masses of the products.)

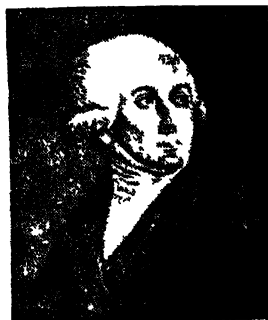


Fig 1(1) Lavoisier

A matter can be chemically transformed into some other substance

or substances having different characteristic properties but the total mass of matter accompanying a chemical change remains unaltered throughout the change. (In other words, *there can be no loss or gain of matter as a result of a chemical reaction.*) As a matter of fact, the chemists have reasons to believe that the total quantity of matter in the universe remains constant and can in no way be altered during the changes taking place in its distribution.

In a physical change also, a matter changes its state of aggregation but the total mass remains the same as before the change has taken place.

For obvious reasons, the law is also called the Law of Indestructibility of matter and may be stated as *“Matter is indestructible and it can neither be created nor destroyed by the application of any process.”*

Let the two substances A and B combine chemically to produce the substances C and D, and if masses a and b of substances A and B react to give masses c and d of substances C and D, then according to this law, $a + b = c + d$.

When iron and sulphur are heated, they combine together to form ferrous sulphide. If x gms of iron combine with y gms of sulphur to form z gms of ferrous sulphide, it will be found that

$$x + y = z.$$

Similarly, when a certain quantity of mercuric oxide (p gms) is decomposed on heating to produce m gms of mercury and n gms of oxygen, then $p = m + n$.

But in certain changes (chemical as well as physical), some apparent anomalies are observed. When a candle burns in air, it gradually diminishes in size and ultimately disappears leaving practically no visible residue behind. A piece of coal on ignition continues burning and finally disappears almost completely. The weight of the residue which is left in the form of ash is much less than that of the original piece of coal. We shall get the same result if a piece of sulphur is similarly ignited in air.

When water is boiled, it entirely disappears. A piece of camphor if left exposed to open air, a diminution in size and weight of the substance is noticed. These are some of the familiar changes where the mass appears to be lost and one may assume that matter has been destroyed in the above cases.

Again, we come across some chemical reactions where the mass appears to be gained. An weighed piece of magnesium on being strongly heated in air burns with a brilliant light and leaves a white residue (ash) which is found to be heavier than the piece of magnesium taken. If a piece of iron of known weight is kept in moist air for some days, it is found that the weight of the piece of iron gets increased. Naturally, these observations may lead to the conclusion that there has been creation of matter in these instances and the law of conservation of mass does not hold good in some cases.

But if the reasons that cause loss or gain to occur in a particular change are explained in the light of transformation of matter, it is found that there is no scope of doubt in the correctness of the law. The failure of the law is only apparent and the law is universally valid. The apparent departure from the law can be explained thus :

(A) The constituent elements of wax of which the candle is made are carbon and hydrogen. During burning, these elements combine chemically with the oxygen of the air producing colourless volatile products—carbondioxide and water vapour respectively both of which disappear in the atmosphere. The candle appears to lose its weight as the colourless gaseous products escape. If the weights of the two gaseous products are taken correctly with the help of suitable means, the same will be found to be equal to the weight of the candle taken and the weight of oxygen consumed during combustion e.g.

Wt. of the wax + wt. of oxygen = wt. of carbon dioxide + wt of water vapour

Thus, it is proved that in the above chemical change, the total mass of the reacting substances remains unaltered.

(B) A piece of camphor is found to lose its weight gradually when kept in open air. Here, the loss in weight is also apparent and in no way contradictory to the law of conservation of mass. Camphor is a volatile solid substance which tends to be converted into its vapour even at the ordinary temperature. Camphor loses its weight as the vapour formed escapes in the atmosphere. If the combined weight of the vapour and the residual solid camphor is taken by a suitable method, it will be found equal to the weight of the piece of camphor originally taken. The conversion of camphor to its vapour is a physical change.

(C) Metallic magnesium gains in weight when ignited in air. The observed gain in weight can easily be explained from the standpoint of the law of conservation of mass. During burning, magnesium unites with the oxygen of the air and is converted into magnesium oxide in the form of a white residue. The residue is found to be heavier as the mass of oxygen which was combined with the metal is included in getting the weight of the product. It can be proved that the weight of magnesium oxide formed is equal to the sum of the weights of magnesium initially taken and the oxygen used up in burning.

(D) A piece of iron, if kept for a long time in moist air, is found to gain in weight. In this case, iron undergoes chemical reaction with oxygen and water vapour and is covered mainly with a layer of brown hydrated ferric oxide called rust. The weight of iron gets increased as some amount of oxygen and water vapour are added to it during rusting.

As a matter of fact, no matter is created or destroyed in any change and the law of conservation of mass holds good in all sorts of chemical (including physical) changes.

Experimental Verification of the Law of Conservation of Mass :

(1) **Lavoisier's Experiment :** (Oxidation of metals) : Lavoisier took a small piece of pure metallic tin in a small retort made of stout

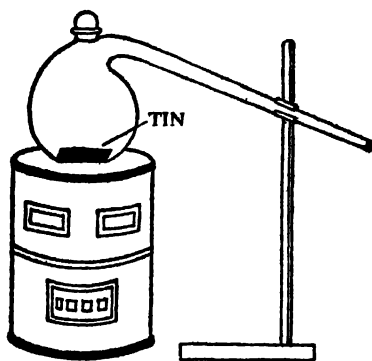


Fig 1(2) Lavoisier's experiment

glass. The mouth of the retort was heated and sealed. The correct weight of the retort with its content was taken and recorded. The retort was then heated for a long time during which a part of the metallic tin was transformed into its oxide by reacting with the oxygen of the air present inside the retort. When the reaction was almost over, heating was discontinued. The closed retort was allowed to cool and weighed again. The weight of the retort was found to remain exactly the same as at first. Thus, the experiment proves that in spite of the conversion of metallic tin to the oxide by a chemical reaction, the total

quantity of matter before and after the reaction, remains unaltered. So in this process, the matter has undergone a change, but no matter has been created or destroyed.

A. B. The experiment when repeated with Cu, Mg or any other oxidisable metal will show the same result.

(2) **Landolt's Experiment :** Landolt carried out a series of experiments which firmly established the truth of the law of conservation of mass. For his experiments, he selected reactions in which the evolution of heat is very small. Solutions of ferrous sulphate and silver sulphate were placed separately in the two limbs of an H-shaped tube which was then sealed by heating. After taking the accurate weight of the tube with its contents, the solutions in the two limbs were mixed up carefully by tilting the tube several times. As a result of a chemical reaction between the solutions of the reactants, metallic silver is precipitated and ferric sulphate is formed.

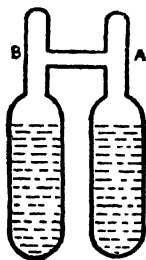


Fig. 1(3)
Landolt's experiment

Silver sulphate + Ferrous sulphate = Silver + Ferric sulphate

When the reaction was over, the H-tube was allowed to cool and weighed again. It was found by Landolt that the weight of the tube remained exactly the same as before. So, it is clear from the experiment that there has been no creation or destruction of matter but merely a redistribution has taken place. The same experiment may

be repeated by taking a solution of silver nitrate in one limb and the solution of sodium chloride in the other. When the solutions are mixed up, a reaction takes place producing white precipitate of silver chloride. Other product formed is sodium nitrate which remains in solution.

Sodium chloride + Silver nitrate = Sodium nitrate + Silver chloride.

(3) **The Charcoal Experiment :** A long necked round bottom flask is fitted tightly with a rubber stopper through which two stout copper wires are passed. One of the wires ends in a spoon and a piece of pure charcoal (sugar charcoal) is kept in it. The other copper wire is introduced in such a way that its end remains very close to the spoon without touching it. The piece of charcoal is wound round by a thin platinum wire which joins the copper wires at their ends. A long glass tube fitted with a stopcock and bent at right angle is then introduced in the flask through the rubber cork. In the upper portion of the neck of the flask, there is a side ube provided also with a stopcock. With the help of the bent tube and the side tube, the flask is filled with oxygen by displacement of air. With the stop-cocks closed, the whole apparatus with its contents is carefully and accurately weighed. Now, the external ends of the copper wires are connected with the terminals of a battery. Thus the electric current is passed through the platinum wire which becomes red hot and the piece of charcoal being in contact with it is ignited and begins to burn to produce colourless carbon dioxide. Under the experimental conditions, carbon dioxide formed cannot escape in the air. When all the carbon has disappeared, the copper wires are disconnected from the battery. The whole apparatus is allowed to cool and weighed again. But it is found that inspite of the transformation of solid charcoal to a colourless gas—carbon di-oxide, the weight of the apparatus remains unchanged.

It was natural for one to expect a loss in weight due to disappearance of charcoal but in reality, it was not so. Thus, the experiment supports the validity of the law of indestructibility of matter.

In place of charcoal, sulphur, phosphorus, magnesium etc., may also be used in the above experiment. In all cases, the non-metals or metals will be converted into their visible or invisible oxides,

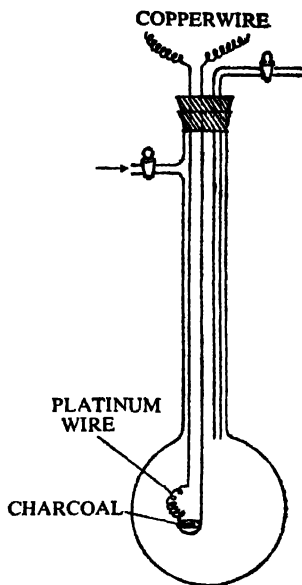


Fig. 1(4) Charcoal experiment

(4) **Experiment on burning of a candle :** (Partington's experiment) : A wide hard glass tube of suitable length is taken. The lower

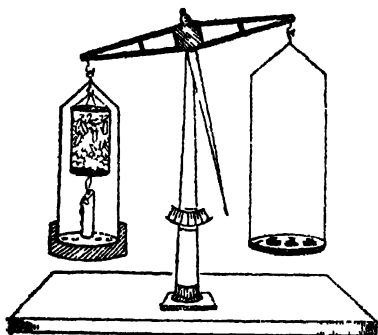


Fig. 1(5) Burning of candle

end of the tube is closed with a perforated cork upon which is placed a small candle. Almost near the other end, the tube is fitted with a copper wire gauze on which a few pieces of quick-lime covered with some caustic soda sticks are kept. On closing the upper mouth of the tube with a suitable rubber cork, the whole apparatus is suspended from the left beam of a balance. The accurate weight of the apparatus is noted. The candle is then lighted and put quickly in its position. The candle burns and a partial vacuum is created inside the tube. As a result, air is drawn in through the perforations of the cork and the regular supply of air keeps the candle burning for some time. As the candle gradually disappears, one can reasonably expect a definite loss in the weight of the apparatus but in practice, the situation is just the reverse. The beam of the balance is inclined in such a way that it records an increase in weight of the tube. This means that the weight gets increased with the gradual disappearance of the candle.

During burning, the constituent elements carbon and hydrogen of the candle combine chemically with oxygen of the air and give off carbon dioxide and water vapour. Under the conditions of the experiment, the gaseous products thus formed cannot escape but are absorbed by the caustic soda and lime kept on the wire gauze. Thus, the tube shows a gain in weight according to the amount of oxygen used up in the combustion. Here, the candle is not destroyed but converted into other substances.

(5) **Experiment on rusting :** A few pieces of clean iron pins (or an iron rod) are kept partly immersed in small quantity of undistilled water taken in a wide glass tube (or a small bottle) as in Fig. 1 (6).

The tube is made air-tight by a tightly fitting cork on its mouth. Now, the closed tube with its contents is accurately weighed and allowed to stand for some days. After a considerable period of time, it is noticed that the iron pins are covered with a thin brown layer (rust). The tube is then weighed again. Although there has been a chemical change, the weight of the tube is found to remain unaltered.

The brown layer appeared on the iron pins is nothing but hydrated ferric oxide (rust) formed as a result of chemical reaction between iron and the moist air inside the tube.



Fig. 1(6)

During rusting, weight of iron pins is increased as oxygen is added to them but at the same time, the amount of oxygen consumed in rusting is decreased from the tube. So, the total quantity of matter before and after the reaction remains the same.

(b) **Experiment on sublimation of camphor :** A small quantity of camphor is taken in a long glass tube, the mouth of which is closed with a tightly fitting rubber cork. The tube with its content is accurately weighed. On heating the tube slightly, the camphor is directly converted into its vapour and is deposited in the form of solid in the upper cooler part of the tube. After cooling to the room temperature, the tube is weighed again. It is found that there is no difference between the two weights (i.e. the weight before heating and the same after heating). This experiment proves that the law of conservation of mass holds good in physical changes too provided arrangements are perfectly made to weigh all the materials before and after the change.

N B Modern idea of radiations has however indicated that the law of conservation of mass is not perfectly true and is true only to a very high degree of approximation. Many chemical reactions are actually accompanied by very slight loss or gain of weight which has been justified from the fact that mass and energy are interconvertible. The equivalence of mass and energy is expressed by Einstein's equation.

$E = mc^2$ where E = energy, m = mass equivalent in gm, c = the velocity of light = 3×10^{10} cm per sec.

So the chemical change where there is an emission of energy, E (usually in the form of heat) will be attended with a corresponding loss of mass equal E/c^2 .

But in such a case also the sum total of mass and energy remains constant. Thus, on the basis of equivalence of energy and mass, the law of conservation of mass may be stated in a modified form as :

The sum of mass and energy in every chemical reaction after the change is exactly the same as the sum of mass and energy before the change.

It is evident from the equation stated above that the change of mass due to conversion to energy is too small (as c is very large) and can safely be neglected in ordinary chemical reactions. ✓

The Law of Definite or Constant Proportions : The law states that :

Every compound is made up of some definite elements combined together in a fixed proportion by weight.

The same compound may be obtained from different sources or can be prepared by application of different methods but it is an established fact that the composition of the particular compound in its pure form is always the same and does not vary with the methods of its preparation or the source from which it is collected. The law further implies that in each and every compound, the constituent elements are present in an invariable weight to weight ratio which is a characteristic of the compound.

Let a particular compound composed of two elements A and B be prepared by three different methods. In the first method, a gms. of A unite with b gms of B, in the second, x gms of A combine with

y gms of B and in the third method m gms of A combine with n gms of B. Then in accordance with the law $\frac{a}{b} = \frac{x}{y} = \frac{m}{n}$ ✓

Illustrations : (1) Water is a compound which can be collected from a well, a river, a sea or from many other natural sources. Moreover, it may be artificially prepared by passing electric spark through a gaseous mixture of hydrogen and oxygen or by passing hydrogen gas over heated cupric oxide. Now, no matter from what source it is obtained or by what method it is prepared, analysis of pure water will reveal that it consists only of two elements, hydrogen and oxygen combined together in the same ratio, 1 : 8 by weight (actually 1.008 : 8). i.e. in water, 1 part by weight of hydrogen is invariably found to combine with 8 parts by the weight of oxygen.

(2) Let us take the case of carbon dioxide. The gas can be prepared in a number of ways as stated below.

- by burning carbon in oxygen
- by heating sodium bicarbonate or calcium carbonate or
- by treating limestone with dil. mineral acids (dil. HCl).

Irrespective of the methods of preparation, carbon dioxide on analysis shows that it contains the elements carbon and oxygen only and the ratio by weight of carbon to oxygen is always fixed i.e. 3 : 8.

✓ **Experimental verification of the Law of Definite proportions :** It is possible to prepare cupric oxide by application of three different methods, such as

Copper nitrate $\xrightarrow{\text{Heated}}$ Cupric oxide + nitrogen dioxide + oxygen

Copper carbonate $\xrightarrow{\text{Heated}}$ Cupric oxide + carbon dioxide

Copper hydroxide $\xrightarrow{\text{Heated}}$ Cupric oxide + water.

Three samples of pure cupric oxide obtained by heating three different compounds of copper are taken and are labelled as sample No. 1, sample No. 2, etc. The constant weight of a clean, dry porcelain boat is determined. A small amount (about 1 gm) of cupric oxide from sample No. 1 is taken in the boat and weighed again accurately. Now the boat with its content is introduced into a hard glass combustion tube clamped in a

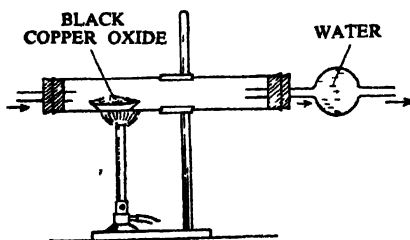
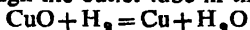


Fig. 1(7) Experiment to verify the law of definite proportions

horizontal position. The mouths of the tube are closed with bored

corks fitted with an inlet and an exit tube. A slow stream of dry and pure hydrogen gas is passed through the inlet tube and the boat is strongly heated. The gaseous hydrogen reduces the heated black cupric oxide to red metallic copper. The water formed as one of the products escapes through the outlet tube in the form of steam.



After the reaction is complete, the heating is stopped. But the flow of hydrogen is continued till the combustion tube is cooled. The boat with copper is taken out, cooled in a desiccator and weighed. The processes of heating, cooling in the desiccator and weighing are repeated until the boat attains a constant weight.

Calculation—Let the wt. of the porcelain boat = W_1 gms

Wt of porcelain boat + Cupric oxide = W_2 gms

Wt of porcelain boat + Copper = W_3 gms

\therefore Wt of cupric oxide = $(W_2 - W_1)$ gms, wt of copper = $(W_3 - W_1)$ gms and the wt of oxygen in cupric oxide = $(W_2 - W_1) - (W_3 - W_1)$ gms = $(W_2 - W_3)$ gms

\therefore Wt of copper = $W_3 - W_1$

\therefore Wt of oxygen = $W_2 - W_3$

\therefore % of copper in cupric oxide = $\frac{100 \times (W_3 - W_1)}{W_2 - W_1}$ and

% of oxygen in cupric oxide = $\frac{100 \times (W_2 - W_3)}{(W_2 - W_1)}$

The same experiment is repeated with cupric oxide from sample Nos-2 and 3. It will be found that within the limits of experimental error, the percentages of copper and oxygen and ratio (by wt) of copper to oxygen in all the samples are the same. Thus the truth of the law of definite proportions is proved.

N.B. It may be noted here that (1) The law of definite proportions is implied in the very definition of a compound. A compound is thus a substance formed by the union of two or more elements in fixed and definite proportions by weight. No compound has ever been known to have a variable composition.

(2) The converse of the law of definite proportions, i.e. the elements combined chemically in a fixed proportion by weight will form the same compound is not always true. It is known that in some cases two or more compounds may have the same composition by weight. The compounds possessing identical chemical composition but having different chemical properties are called isomers.

and the phenomenon is known as isomerism. Urea $\left(\text{O}=\text{C} \begin{matrix} \text{NH}_2 \\ \text{NH}_2 \end{matrix} \right)$

and ammonium cyanate (NH_4CNO) are found to contain the same elements combined in the same weight ratios but they are entirely different compounds with different properties. The existence of isomers is frequently observed in organic compounds.

(3) Discovery of isotopes of elements has set a limit to the validity of the law. It is now known that most of the ordinary elements consist of a mixture of isotopes, i.e. the atoms with identical chemical properties but with different atomic weights (mass) and these differences in atomic weights may significantly effect the chemical composition of a substance. For example, two isotopic forms of hydrogen called ordinary and heavy hydrogen are known. The atoms of heavy hydrogen weigh twice as much as of the ordinary hydrogen. Thus, if water contains varying proportions of the two varieties of hydrogen, its composition by weight may not always be the same. Again, oxygen exists in

atleast three isotopic forms with atoms of different weights i.e. 16, 17 and 18. Consequently, a specimen of cupric oxide containing a predominating amount of one particular isotope of oxygen will have a composition by weight slightly different from a specimen which contains more of another isotope. Of course, such variation in composition is very rarely met with. By and large, the relative proportions of the various isotopes in any compound remain the same. As a result, the composition of the compound by weight remains unaltered and the law of constant proportions generally holds good. However, the existence of isotopy, necessitates some modification in the statement of the law. The modified form of the law of constant or definite proportions is as follows.

A given chemical compound always contains the same isotopes or a mixture of isotopes of the constituent elements united in the same definite proportions by weight.

Law of Multiple Proportions: The law states: When two elements combine chemically to form two or more compounds, the different weights of one of the elements that combine with a fixed weight of the other element bear to each other a simple ratio of small whole numbers.

Illustrations (1) When combined chemically, hydrogen and oxygen form two different compounds, viz. water and hydrogen peroxide.

In water, 2 parts by weight of hydrogen combine with 16 parts by weight of oxygen and in hydrogen peroxide, 2 parts by weight of hydrogen combine with 32 parts by weight of oxygen. (It is better to say 2.016 parts by wt. of hydrogen.)

So, it is found that different weights of oxygen (viz. 16 and 32 parts) which unite with a fixed weight (2 parts) of hydrogen to form the compounds referred to are in the ratio of 16 : 32 or 1 : 2 which is a simple ratio of small whole numbers.

Alternatively, the different weights of hydrogen that combine with the constant weight of oxygen (16 parts) are in the ratio of 2 : 1.

(2) Carbon and oxygen combine together to form two oxides, carbon monoxide and carbon dioxide. Chemical analysis shows that in carbon monoxide, ratio of the weights of carbon to oxygen is 12 : 16. Again in carbon dioxide, the ratio of the weights of carbon to oxygen is 12 : 32.

∴ The weights of oxygen which combine with the same weight of carbon to form these oxides bear to one another the simple ratio 16 : 32 or 1 : 2. In a similar manner, it is found that the different weights of carbon that combine with the fixed weight of oxygen (16 parts) are in the ratio of 12 : 6 or 2 : 1.

(3) Nitrogen forms as many as five stable oxides and it is found that the composition of the oxides of nitrogen illustrates the law of multiple proportions.

Compounds	Composition by weight	
	Nitrogen : Oxygen	Nitrogen : Oxygen
(a) Nitrous oxide	28 : 16	14 : 8
(b) Nitric oxide	14 : 16	14 : 16
(c) Nitrogen trioxide	28 : 48	14 : 24
(d) Nitrogen dioxide	14 : 32	14 : 32
(e) Nitrogen pentoxide	28 : 80	14 : 40

The different weights of oxygen combining with a definite weight (14 parts) of nitrogen are in the ratio of 8 : 16 : 24 : 32 : 40 or 1 : 2 : 3 : 4 : 5. This is a simple integral ratio in accordance with the law.

(4) The result of chemical analysis of two compounds formed by iron and chlorine is as follows

Compounds	Ratio of weights Iron . Chlorine
(a) Ferrous chloride	56 : 71
(b) Ferric chloride	56 : 106.5

Hence the different weight of chlorine (viz 71 and 106.5 parts) which unite with a fixed weight of iron (56 parts) are in the simple ratio of 2 : 3.

(5) The analytical result of the three oxides of lead is given below

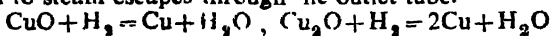
Compounds	Lead : Oxygen	Ratio of weights
(a) Litharge	107.2 16	107.2 16
(b) Lead peroxide	107.2 32	53.6 16
(c) Red lead	321.6 64	80.4 16

Hence, 16 parts by weight of oxygen combine respectively with 107.2, 53.6 and 80.4 parts by weight of lead. It means that a simple ratio 4 : 2 : 3 exists between the weights of lead that combine with the same weight of oxygen.

Experimental verification of the law of Multiple proportions :
We know that copper and oxygen combine together to form two oxides viz, black cupric oxide (CuO) and red cuprous oxide (Cu_2O).

The constant weights of two dried, well-cleaned porcelain boats are determined. In one of them (say boat No 1), a little dry and pure sample of cupric oxide and in the other (boat No 2), a little dry and pure sample of cuprous oxide are taken. The accurate weights of the two boats with their contents are taken separately. Two boats with the different oxides are then placed side by side in a hard glass combustion tube clamped horizontally. Both the open ends of the combustion tube are closed with two corks through which two glass tubes are attached. One of the tubes is used as an inlet for hydrogen and the other as an outlet for steam.

Now, the boats are very strongly heated by means of Bunsen burners while a slow stream of dry and pure hydrogen is passed through the inlet tube. Under the experimental conditions, hydrogen reduces both the copper oxides to metallic copper and itself being oxidised to steam escapes through the outlet tube.



When the reaction is complete, heating is stopped. The flow of hydrogen is maintained for sometimes while the combustion tube and the boats are allowed to cool. The two boats are then taken out, cooled in a desiccator and accurate weights of the boats with their contents (metallic copper) are taken.

Calculations : Let the wt. of porcelain boat No 1 = W_1 gms.

Constant wt. of boat No 1 + Cupric oxide = W_2 gms.

Copper = W_3 gms.

∴ Wt. of "cupric oxide" " " " + = $(W_2 - W_1)$ gms.

and wt. of copper = $(W_3 - W_1)$ gms.

∴ Wt of oxygen in cupric oxide = $(W_2 - W_1) - (W_3 - W_1)$
= $(W_2 - W_3)$ gms.

That is to say, $(W_2 - W_3)$ gms of oxygen combine with $(W_3 - W_1)$ gms of copper to form cupric oxide.

∴ 1 gm of oxygen will combine with $\frac{W_3 - W_1}{W_2 - W_3}$ gms or x gms of copper.

Similarly, let the constant wt of boat No 2 = a gms

Wt of boat No 2 + Cuprous oxide = b gms

Wt of boat No 2 + Copper = c gms

∴ Wt of copper = $(c - a)$ gms and wt of oxygen = $(b - c)$ gms

So, $(b - c)$ gms of oxygen unite with $(c - a)$ gms of copper to form cuprous oxide.

∴ 1 gm of oxygen will combine with $\frac{c - a}{b - c}$ gms or y gms of copper.

Experimental results show that the ratio of the different weights of copper (x and y gms) in the two oxides combining with the fixed wt of oxygen will come out as 1 : 2. Thus, the law is experimentally verified. ✓

N. B. When the compounds formed by the chemical combination of two elements are many and are not simple chemically, the ratio worked out as above may not remain of small whole numbers. As for example, carbon and hydrogen can form a large number of compounds called hydrocarbons. When the hydrocarbons butane, pentane and hexane are analysed, it is found that 12 parts by weight of carbon combine respectively with 2.5, 2.4 and 2.33 parts by weight of hydrogen. These figures clearly do not have a simple ratio of small whole numbers. Again, the analytical results of methane and decane show that the amounts of hydrogen that combine with a definite quantity of carbon in these two compounds are in the ratio of 20 : 11. This can hardly be regarded as a simple ratio of small integers.

It should also be kept in mind that the law of multiple proportions as stated earlier is strictly applicable only if we consider such compounds which are formed from the same isotopes of the concerned elements or from a mixture of the isotopes of fixed composition.

✓ **The Law of Reciprocal proportions :** The law is enunciated thus : The weights of two or more different elements which separately combine with a fixed weight of another element are either the same as or are simple multiples or submultiples of the weights of these different elements when they combine with each other. In other words the proportions in which any two elements combine with a third element are the proportions or a simple multiple (or submultiple) of the proportions in which they combine amongst themselves.

Explanation : Let a and b gms of two different elements X and Y respectively react with c gms of another element Z . Now if X and

X and Y combine together, the ratio by weight in which they do so will either be $a : b$ or a simple multiple of the ratio of the weights of X and Y which combine with a constant weight of Z i.e. $ma : nb$ (where m and n are simple, whole numbers).

Illustrations : (1) The elements carbon and oxygen combine with hydrogen separately to form methane and water respectively. Chemical analysis reveals that in methane, the ratio of the wts of hydrogen to carbon is 4 : 12 or 1 : 3. Again, in water, the weight ratio of hydrogen to oxygen is 1 : 8. Thus, in two compounds, 3 parts by weight of carbon and 8 parts by weight of oxygen have separately combined with a constant weight of hydrogen (1 part).

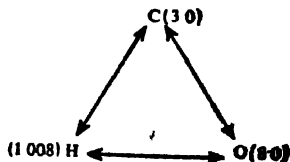


Fig. 1(8)

According to this law, if carbon and oxygen combine at all, they must do so either (i) in the ratio of 3 : 8 or (ii) in its simple multiples (or sub-multiples). Now carbon is known to combine with oxygen to give two different compounds—carbon dioxide and carbon monoxide. In carbon dioxide, the ratio of the weights of carbon to oxygen is 12 : 32 or 3 : 8, which is the same as predicted by the law. In carbon monoxide, 12 parts by weight of carbon unite with 16 parts by weight of oxygen.

∴ the weight ratio of carbon to oxygen is 12 : 16 or 6 : 8 (6 is a multiple of the first i.e. 3). This has been depicted clearly in fig. 1 (8) taking $H = 1.008$.

(2) The two elements oxygen and sulphur separately combine with carbon to give two compounds—carbon dioxide and carbon disulphide.

In carbon dioxide, wt of carbon : wt of oxygen = 12 : 32 and in carbon disulphide, wt of carbon : wt of sulphur = 12 : 64. Therefore, sulphur and oxygen should combine in the ratio of 64 : 32 or 2 : 1 or in their simple multiples. We know that sulphur combines with oxygen to give two oxides—sulphur dioxide and sulphur trioxide.

In sulphur dioxide, wt of sulphur : wt of oxygen = 32 : 32 or 2 : 2 or 2 : 1 $\times 2$ (a multiple of the latter) and in sulphur trioxide, wt of sulphur : wt of oxygen = 32 : 48 or 2 : 3 i.e. 2 : (1 $\times 3$) [3 is a multiple of 1].

(3) 31 parts by the weight of phosphorus combine with 3 \times 35.5 parts by the weight of chlorine to form the compound phosphorus trichloride and 31 parts by weight of phosphorus and 3 parts by weight of hydrogen react together to form the compound named phosphine. The weights of hydrogen and chlorine which combine with the same weight, viz. 31 parts of phosphorus, are in the ratio 3 : 106.5 or 1 : 35.5. Therefore if hydrogen and chlorine happen to combine chemically, they will do so in the proportion of 1 : 35.5 or its simple multiples. Actual experiment shows that the weight

ratio of hydrogen to chlorine in hydrogen-chloride is 1 : 35.5 which illustrates the law.

N.B. An important consequence of the law of reciprocal proportions is the emergence of the idea of combining weights or equivalent weights and this is why *this law may be taken as a special case of law of equivalent proportions*. This law for the first time pointed to the relationship between the weights of various elements when they combine amongst themselves.

It is found that oxygen can easily combine with very many elements and if we analyse some of the binary compounds of oxygen, we find that

8 parts by wt. of oxygen combine with 1.008 parts by wt. of hydrogen
8 parts by wt. of oxygen combine with 35.46 parts by wt. of chlorine
and 8 parts by wt. of oxygen combine with 20.00 parts by wt. of calcium.

Now if the fixed weight referred to in the statement of the law is 8.00 parts by wt. of oxygen, the elements on the right hand side shall combine (if they combine at all) in the proportions of the said wts or simple multiples thereof. Analytical data reveal that 20.0 parts by wt. of calcium will combine with 1.008 parts by wt. of hydrogen or 35.46 parts by wt. of chlorine.

The numerical figures given in the bracket [vide fig 1 (9)] are called the equivalent or combining weights of the elements and it will be evident that the elements when combine will do so in the proportion of their combining weights. The subject will be discussed in detail in chapter 5 (Group A) of this book.

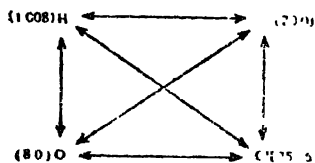


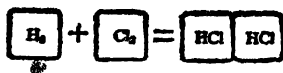
Fig 1(9)

Law of gaseous volumes or Law of combining volumes—Gay Lussac's law: Gay Lussac in a

large number of experiments with gases noted their volumes and enunciated a law of chemical combination known as Gay Lussac's law. The law states—Under the same conditions of temperature and pressure, two or more gases combine chemically in simple ratios by volumes and the volumes of the products if gaseous also bear a simple relation to the volumes of the reacting gases.

Illustrations: Actual experiments show that under the identical conditions of temperature and pressure—

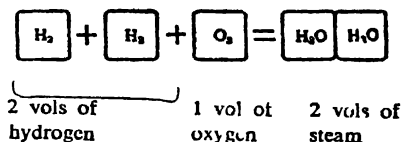
(1) 1 vol. of hydrogen and 1 vol. of chlorine combine chemi-



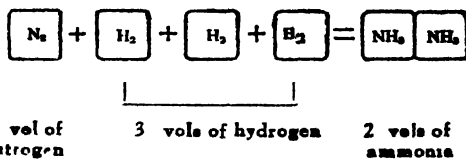
1 vol of 1 vol of 2 vols of
hydrogen chlorine hydrogen chloride

cally to give 2 vols of hydrogen chloride. Thus, the ratio of the vols of these gases is $H : Cl : HCl = 1 : 1 : 2$, which is a simple ratio in accordance with the law. ✓

(2) 2 vols of hydrogen and 1 vol. of oxygen on chemical combination produce 2 vols of steam. ∴ Vols of the reacting gases and the product bear a simple ratio to one another i.e. $2 : 1 : 2$:



(3) 1 vol. of nitrogen and 3 vols of hydrogen combine to form 2 vols of ammonia ∴ ratio of the vols of the gases is $1 : 3 : 2$. Thus, the above examples prove the validity of the law beyond any doubt.



Of the laws of chemical combination, only Gay Lussac's law deals with the vols of the reacting gases and it will be shown shortly that this law cannot be explained with the help of Dalton's atomic theory

✓ **Constitution of matter—Dalton's Atomic theory** The idea that matter is composed of extremely small and indivisible particles was even held by the early Greek and Indian philosophers. In fact, the term 'atom' for such a particle originated from the Greek meaning 'not divided'. However, John Dalton was the first scientist to give a definite shape to the concept of the early thinkers and proposed a theory concerning the ultimate constitution of matter. This theory is called Dalton's atomic theory.

It is a fact that in the light of present scientific information, the theory is no longer acceptable in its original form and some of its assumptions have already undergone modification. But Dalton's atomic theory is still regarded as the very foundation of the development of modern sciences in general and chemistry in particular



Fig. 1(10)
John Dalton

✓ **Basic assumptions or postulates of Dalton's atomic theory :**

(1) Every matter is discrete and is made up of indefinitely small, real particles called atoms which are incapable of being subdivided. In other words, atoms are the smallest ultimate particles that build up a matter.

(2) Atoms of an element cannot be created, destroyed or changed into another in course of a chemical change.

(3) All the atoms of the same element are equal in weights, size etc., and possess identical properties. Atoms of different elements have different weights and different characteristic properties. The properties of matter denote the properties of its atoms.

(4) Chemical combination between two or more reacting elements results from the union of atoms of these elements in definite numerical proportions i.e. in simple ratio of whole numbers such as 1 : 1, 1 : 2, 2 : 3 etc.

(5) The ratio of the combining weights of the constituent elements in a compound represents the ratio of the combining weights of their atoms.

According to Dalton, an atom is the smallest indivisible particle of an element which can take part in a chemical change.

Critical study of the theory—Explanation of the laws of chemical combination in the light of Dalton's atomic theory :

Various laws of chemical combination by weight can be explained in a simple and convincing way with the help of Dalton's atomic theory.

✓ (A) *The law of Indestructibility of matter or law of conservation of mass :* According to Dalton's atomic theory, matter is composed of its innumerable number of atoms which cannot be created, destroyed or subdivided during a chemical change. The theory also demands that an atom is a definite particle with a definite mass.

A chemical reaction simply involves redistribution or rearrangement of various atoms of matter and the total number of atoms taking part in a chemical process before and after the change will remain unaltered. If it is so, the sum of the masses of the constituent atoms of the reacting substances will be equal to the masses of the atoms of the products. This implies that the total mass of a chemical system will remain constant. It is exactly what the law of conservation of mass signifies.

✓ (B) *The Law of Definite or Constant proportions :*

Dalton's atomic theory states that a chemical compound is always formed by the union of atoms of two or more elements in a fixed ratio of simple whole numbers. As every atom of an element has a fixed weight, it means that the constituent elements of a compound must essentially bear a constant ratio by weight.

Let two elements A and B chemically combine to form a compound and let x atoms of A unite with y atoms of B to give the compound A_xB_y . Now if a and b stand respectively for the weight of one atom of A and one atom of B, then in the compound A_xB_y , x , y are always definite whole numbers and a , b are also invariable or constants.

So, the compound under consideration will contain ax parts by the weight of A and by parts by the weight of B. In other words, the ratio of the relative weights of the combining elements A and B in the compound A_xB_y is constant

$$\text{i.e., } \frac{\text{Wt. of A}}{\text{Wt. of B}} = \frac{ax}{by} = \text{Constant.}$$

In this way, we can arrive at the conclusion that each compound has an invariable composition. Thus, the law of definite or constant proportions is explained logically by Dalton's atomic theory.

✓(C) *The Law of Multiple Proportions* : Let two elements A and B combine chemically and form more than one compound. The atoms are indivisible and according to Dalton's atomic theory, the formation of each of the compounds of A and B will take place by chemical interaction of an integral number of atoms of A with an integral number of atoms of B or the compounds are formed by the union of atoms of two elements in simple numerical proportions.

Let us suppose further that 1 atom of A combines with 1 atom of B to give the compound AB; 1 atom of A combines with 2 atoms of B to form the compound AB_2 , and 2 atoms of A combine with 3 atoms of B to give the compound A_2B_3 . Let a and b denote the weight of 1 atom of A and that of one atom of B respectively. Since all atoms of the same element possess equal weight, a and b must have fixed values.

(i) Now in the compound AB,

a parts by wt. of A combine with b parts by wt. of B.

(ii) in the compound AB_2 ,

a parts by wt. of A unite with $2b$ parts by wt of B and

(iii) in the compound A_2B_3 ,

$2a$ parts by wt of A combine with $3b$ parts by wt of B.

or a parts by wt of A combine with $\frac{3b}{2}$ parts by wt of B

Therefore, the wts of B which combine with a fixed or constant wt of A (a part) are as $b : 2b : \frac{3b}{2}$ or, $1 : 2 : \frac{3}{2}$ or, $2 : 4 : 3$ which is a simple ratio of small whole numbers. Thus the law of multiple proportions is explained and proved from Dalton's theory.

✓(D) *The Law of Reciprocal Proportions* :

Let a , b and c represent the weight of 1 atom of each of the three elements A, B, and C respectively. Let us suppose that 1 atom of A combines with 1 atom of B to give a compound AB and 1 atom of A can separately combine with 1 atom of C to form a compound AC. Therefore, a parts by the wt of A separately combine with b parts by the wt of B and c parts by the wt of C. Now if B and C combine together, then atoms being indivisible, the resulting compound will consist of either (i) at least 1 atom of B and 1 atom of C to give the compound BC or (ii) x atoms of B and y atoms of C to form the compound B_xC_y (x and y are positive integers). We know that the atoms of an element have invariable weight. So in the first case, in

the compound BC, b parts by wt of B combine with c parts by wt of C.

Thus, it is found that the wts. in which B and C themselves combine are the same as the weights in which B and C separately combine with the constant weight (a part) of A.

In the second case, the compound B_xC_y would contain $b \times x$ parts by the wt of B and $c \times y$ parts by the wt of C. Now $b \times x$ and $c \times y$ are simple multiples of ' b ' and ' c ' respectively as x and y are small positive integers. Hence the weights in which B and C combine together are simple multiples of the weights in which B and C separately combine with the constant weight (a part) of A.

This leads to the conclusion that combining weights of two elements are either the same or simple multiples of the weights in which they combine with the fixed weight of a third element and hence the law is derived from Dalton's atomic theory.

Importance of Dalton's Atomic theory :

(1) The atomic theory as introduced by John Dalton marks the inception of a new era in chemical thinking and is the first attempt to place the corpuscular concept of matter upon a scientific basis. The quantitative concept of matter during a chemical change is also derived from the theory.

(2) Dalton's atomic theory succeeds in explaining the laws of chemical combination with the exception of law of gaseous volumes.

(3) The postulate that the atoms of the same element are identical with each other in weights and show similar properties help in expressing the chemical reactions by equations. With the introduction of atomic weights, the calculations as to the relative masses of substances entering into a chemical combination become easier.

(4) The assumption of Dalton that the atom is the smallest unit in all chemical reactions gave the impetus to subsequent researches in chemistry.

Limitations of Dalton's Atomic theory—its present position :

(1) According to Dalton, an atom stands for the smallest particle of any kind of matter. He did not make any distinction between the smallest particles of an element and a compound. The indiscriminate use of the word 'atom' subsequently led to serious complications.

(2) The theory fails to explain at least one of the fundamental laws of chemical combination i.e., Gay Lussac's law of gaseous volumes.

(3) The assumption that the atom is the ultimate indivisible particle of matter is not supported by modern investigations. The complexity of the atom became increasingly apparent with the discovery of radioactivity, various types of radiations, electrons, and a number of sub atomic particles. It is now proved beyond any doubt that an atom is composed of some other smaller particles like electron, proton, neutron, positron etc. Further, modern discoveries have proved that the atoms really get divided during nuclear reactions, radio active changes, electrical discharges etc.

It is now known that chemical combinations take place by the

shifting of electrons from one atom to other. So, strictly speaking, even in a chemical change, the atom is not indivisible. But since the transference of electrons does not cause any appreciable change in the weight of the atom, the indivisibility of the atom is not seriously affected and we may safely take that atoms are indivisible in chemical reactions. (4) The important postulate that the atoms of the same element are identical with each other in weight has also been proved erroneous with the discovery of isotopes. It is now known that atoms of the same element having different atomic weights may exist. Further, the discovery of isobars has proved that the atoms of different elements with altogether different chemical properties may have the same atomic weight.

✓ **Atomic weight :** One of the postulates of Dalton's atomic theory is that the atom of a given element has a definite and constant weight. Atoms are extremely minute particles and the actual weight (mass) of an atom is too small to be determined by direct weighing. It has been calculated that the actual weight of one atom of the lightest element hydrogen is 1.66×10^{-24} gm, and that of uranium, the heaviest stable element, is 3.85×10^{-22} gm only. So, for all practical purposes, these insignificant quantities cannot be suitably used in chemical calculations. But the difficulties in this respect are overcome if the comparative values for the weights of the atoms of the different elements are used instead of their actual weights. Moreover, it is convenient to determine the weight of one atom of an element relative to that of an atom of a standard element which has been assigned a definite value. Accordingly,

Atomic weight of an element

$$= \frac{\text{weight of one atom of the element}}{\text{weight of one atom of the standard element}}$$

Thus, the atomic weight is a ratio. It does not signify the actual weight of an atom of the element and has no unit.

Initially, the weight of an atom of hydrogen, the lightest known element, was chosen as the standard for comparison by Dalton and the weight of one atom of hydrogen was taken as 1. Thus,

✓ The atomic weight of an element expresses a number which shows how many times an atom of the element is heavier than one atom of hydrogen, taking the weight of an atom of hydrogen as unity.

The atomic weight of nitrogen is 14. It means that the weight of one atom of nitrogen is 14 times the weight of one hydrogen atom. On the same standard, the atomic weights of chlorine, sulphur, sodium are 35.5, 32.00 and 23.00 respectively.

Subsequently, it was found more convenient to take oxygen as the standard for determining the atomic weights of other elements (the atomic weight of oxygen taken to be 16.00). So on the oxygen standard or oxygen scale, the atomic weight of an element is defined as follows :

✓ The atomic weight of an element is the weight of an atom of the element as compared with the weight of one atom of oxygen taken as

16.00. Alternatively, the atomic weight of an element is a number which represents how many times an atom of the element is heavier than one sixteenth part of the weight of an oxygen atom.

$$\therefore \text{Atomic weight} = \frac{\text{weight of one atom of the element}}{\frac{1}{16} \text{th part of the weight of one oxygen atom}}$$

$$= \frac{\text{weight of one atom of the element}}{\text{weight of one atom of oxygen}} \times 16$$

Here, $\frac{1}{16}$ th part of the weight of an oxygen atom has been taken as unit of comparison. On this scale, the atomic weights of hydrogen, chlorine, carbon, nitrogen, sodium are 1.008, 35.457, 12.01, 14.008, 22.997 respectively.

✓ **Reasons for acceptance of oxygen as standard :** (1) It is much more easy to prepare compounds with oxygen than with hydrogen. Generally hydrogen does not form well defined compounds with metals.

(2) If hydrogen atom, the lightest of all elements, is used as a standard for comparison, small experimental errors are likely to be magnified.

(3) The atomic weights of most elements come very near to whole numbers when oxygen is taken as 16.00. But this is not the case when hydrogen is taken as a substance for comparison.

The oxygen 16.000 standard remained in use until 1961 when it was replaced. At present, carbon atom with its weight (mass) equal to 12.00 has been accepted as the standard of determining atomic weights in place of oxygen. Therefore, the atomic weight according to the modern standard, is defined thus—

✓ **The relative weight of one atom of an element with respect to the weight of one carbon atom taken as 12.00 is referred to as the atomic weight of the element.** Here, one-twelfth part of the weight of a carbon atom ($C=12$) has been taken as the unit.

The acceptance of $C=12$ as the standard in lieu of $O=16$ was an outcome of the discovery that ordinary oxygen consists of a mixture of three isotopes weighing 16, 17 and 18 on the oxygen atomic weight scale. The oxygen 16.000 standard was then considered to be unsuitable since the standard ($O=16$) itself represented only an average weight of the mixture of natural isotopes constituting the gaseous oxygen and the atomic weight of any element would depend on the isotopic composition of oxygen employed as the standard. It was reasonably thought to choose a single isotope of an element as the standard which would remain perfectly constant. The carbon-12 isotope, the commonest isotope of carbon, has finally been selected as the present standard. This standard has an additional advantage that its adoption has least affected the values of atomic weights of various elements determined on the basis of old oxygen scale. As for example, on the new carbon scale, the atomic weight of oxygen is 15.999415. This makes a very little difference. ✓

In the light of isotopy, the atomic weight is the average relative

weight of one atom of an element as compared with the weight of a carbon-12 isotope.

The word 'average' in the above definition covers all the isotopic forms of the same element. The atomic weight of an element is the average of the relative weights of all its isotopes. For example, the atomic weight of chlorine is 35.46. It signifies the average relative weight of one atom of chlorine as ordinary chlorine consists of two kinds of isotopes present in the proportion of about 3 : 1 having atomic weights 35 and 37.

The smallest weight of the element present in a number of compounds formed by it may also be called the atomic weight of the element.

The students at the Higher Secondary stage may use the values of atomic weights obtained on the oxygen scale. Even for simplicity in chemical calculations, the beginners are sometimes allowed to use $H=1$, $Cl=35.5$, $N=14$ etc.

Atomic mass unit (a m. u) : Nowadays, atomic mass unit has been introduced to express the mass of a single atom of the respective element where,

$$1 \text{ amu} = \frac{1}{6.023 \times 10^{23}} \text{ gm} = 1.6603 \times 10^{-24} \text{ gm}$$

$$= \frac{1}{12} \text{th of the mass of a carbon atom}$$

Mass of a hydrogen atom = 1.008 amu

$$= 1.008 \times 1.6603 \times 10^{-24} \text{ gm}$$

$$\text{Or, } 1.673 \times 10^{-24} \text{ gm.}$$

Mass of one oxygen atom = 16 amu = $16 \times 1.6603 \times 10^{-24} \text{ gm.}$

$$= 2.66 \times 10^{-23} \text{ gm.}$$

Gram-atomic weight or gram-atom : A quantity in grams which is numerically equal to the atomic weight of an element is known as the gram atomic weight of the particular element. In short, **gram atomic weight or gram-atom of an element is its atomic weight expressed in grams.**

Thus, 16 gms of oxygen stand for one gram-atom of oxygen. 1 gm-atom of hydrogen = 1.008 gms of hydrogen, 1 gm-atom of carbon = 12.00 gms of carbon.

Numerical examples

On the law of Definite Proportions :

(1) 'C' is a compound. 30 gms of it on analysis give 10 gms of an element 'A' and 20 gms of another element 'B'. If 15 gms of A and 50 gms of B are mixed and reacted, what weight of C will be produced and what will be the total weight of the mixed substances.

[W. B. H. S. 1980]

30 gms of 'C' on analysis give 10 gms of A and 20 gms of B.

∴ According to the law of definite proportions,

$$\frac{\text{Weight of A}}{\text{Weight of B}} = \frac{10 \text{ gms}}{20 \text{ gms}} = \frac{1}{2}$$

Or, the ratio between the weights of A and B is 1 : 2

So, 15 gms of A combine with 2×15 or 30 gms of B to give 15 + 30 or 45 gms of C. and the amount of B remaining unreacted = $50 - 30 = 20$ gms.

∴ Total weight of the mixed substances = $45 + 20 = 65$ gms.

(2) Silver chloride obtained by three different methods gave the following results on analysis :—

- (i) 79.95 g. of silver chloride contain 60.18 g. of silver
- (ii) 108.1552 g. of silver chloride contain 81.411 g. of silver
- (iii) 69.6558 g. of silver chloride contain 52.423 g. of silver

Show that these figures illustrate the law of constant proportions.

In sample (i),

79.95 g. of silver chloride contain 60.18 g. silver

∴ 100 g. of silver chloride contain $\frac{60.18 \times 100}{79.95}$ or 75.272 g. silver

∴ 100 g. of silver chloride contain $(100 - 75.272)$ or 24.728 g. chlorine.

In sample (ii),

108.1552 g. of silver chloride contain 81.411 g. of silver

∴ 100 g. of silver chloride contain $\frac{81.411 \times 100}{108.1552}$ or 75.271 g. silver

∴ 100 g. of silver chloride contain $(100 - 75.271)$ or 24.729 g. chlorine.

In sample (iii)

69.6558 g. silver chloride contain 52.423 g. silver

∴ 100 g. silver chloride contain $\frac{52.423 \times 100}{69.6558}$ or 75.26 g. silver

∴ 100 g. silver chloride contain $(100 - 75.26)$ or 24.74 g. chlorine

The percentages of chlorine and silver in all the three samples are the same. So, the figures illustrate the law of constant proportions

(3) Given that (a) 1.316g of zinc gave 1.6394g of zinc oxide when heated in air ; (b) 1.30g of zinc was dissolved in nitric acid. The resulting zinc nitrate on ignition gave 1.620g zinc oxide. (c) 2.646g of a sample of zinc oxide was reduced by heating in a current of hydrogen and the weight of zinc that remained was 2.124g. Show that the results agree with the law of constant proportions.

From the data given,

(a) Weight of zinc oxide produced = 1.6394g

Weight of zinc = 1.316g

∴ Weight of oxygen in zinc oxide = $(1.6394 - 1.316)g = 0.3234g$.

∴ $\frac{\text{Weight of zinc}}{\text{Weight of oxygen}} = \frac{1.316}{0.3234} = 4.069$

(b) Weight of zinc oxide produced = 1.620g

Weight of zinc used = 1.30g

∴ Weight of oxygen in zinc oxide = $(1.620 - 1.30)g$ or 0.320g.

∴ $\frac{\text{Weight of zinc}}{\text{Weight of oxygen}} = \frac{1.30}{0.320} = 4.062$

- (c) Weight of zinc oxide = 2.646 g ;
 Weight of Zn produced = 2.124 g
 \therefore Weight of oxygen = (2.646 - 2.124) g or 0.522 g.
 $\therefore \frac{\text{Weight of zinc}}{\text{Weight of oxygen}} = \frac{2.124}{0.522} = 4.069$

The above calculations show that the ratio of weights of zinc to oxygen in zinc oxide obtained by different methods is same. So, the results agree with the law of constant proportions.

(4) Given that (i) 0.36 gm. of a metal when burnt in oxygen yields 0.60 gm. oxide ; (ii) carbonate of that metal contains 28.57% of the metal. Determine with the help of the law of definite proportions, the wt. of the oxide which will be obtained by heating 1 gm. of that carbonate.

Given, wt. of the oxide of the metal = 0.60 gm.

Wt. of the metal = 0.36 gm.

\therefore Wt. of oxygen = (0.60 - 0.36) gm. or 0.24 gm.

\therefore The metal to oxygen ratio in the oxide

$$= \frac{\text{Wt. of the metal}}{\text{Wt. of oxygen}} = \frac{0.36}{0.24} = \frac{3}{2}$$

Again, percentage of the metal in the carbonate is 28.57

100 gms. of the carbonate contain 28.57 gms. of the metal

\therefore 1 gm. of the carbonate contain 0.2857 gm of the metal

Now, according to the law of definite proportions, the ratio of the metal to oxygen in the oxide obtained in different methods is 3 : 2,

$$\therefore \frac{\text{Wt. of the metal}}{\text{Wt. of oxygen}} = \frac{3}{2} \quad \text{or} \quad \frac{0.2857}{\text{Wt. of oxygen}}$$

$$\therefore \text{Wt. of oxygen} = \frac{2 \times 0.2857}{3} \text{ g.} = 0.1905 \text{ gm.}$$

Hence, the amount of the oxide that will be obtained from 1 gm. of the carbonate = (0.2857 + 0.1905) gm.

$$= 0.4762 \text{ gm.}$$

On the Law of Multiple Proportions :

(5) Metal M and chlorine combine in different proportions to form two compounds A and B. The mass ratio M : Cl is 0.895 : 1 in A, and 1.791 : 1 in B. What law of chemical combination does this example illustrate ?

1 part of chlorine combines with 1.791 and 0.895 parts of M in compounds B and A respectively.

$$\therefore \frac{\text{M in B}}{\text{M in A}} = \frac{1.791}{0.895} = \frac{2}{1} \text{ i.e., a simple ratio.}$$

So, the result illustrates the law of multiple proportions.

(6) Copper forms two oxides. 1.00 gm. of copper was dissolved in nitric acid and on ignition gave 1.25 gm. of cupric oxide. 1.00 gm. of cuprous oxide when ignited in a current of hydrogen gave 0.888

gm. of copper. Show that these results illustrate the law of multiple proportions.

From the data given,

Weight of cupric oxide produced = 1.25 gms,

Weight of copper used = 1.00 gm.

∴ Weight of oxygen in cupric oxide = 0.25 gm.

0.25 gm. of oxygen combines with 1.00 gm of copper

∴ 1 gm. of oxygen combines with $\frac{1}{0.25} = 4.0$ gms, copper

We know that when an oxide is heated in a current of hydrogen the metal is produced by removal of oxygen.

In cuprous oxide,

(1 - 0.888) or 0.112 gm. of oxygen combines with 0.888 gm. of copper

∴ 1 " " " " " " " $\frac{0.888}{0.112} = 7.9$ gms

of copper

The ratio of the different wts. of copper combining with a fixed weight of oxygen (1 gm.) is 4 : 7.9 i.e., 1 : 2 which is a simple ratio. Thus, the results illustrate the law of multiple proportions.

(7) Phosphorus is found to form three oxides containing respectively 43.668, 49.212 and 56.365 per cent of phosphorus. Show that these figures illustrate the law of multiple proportions.

The first oxide contains 43.668% of Phosphorus

and (100 - 43.668) or 56.332% of Oxygen

The second oxide contains 49.212% of Phosphorus

and (100 - 49.212) or 50.788% of Oxygen.

The third oxide contains 56.365% of Phosphorus

and (100 - 56.365) or 43.635% of Oxygen.

In the first oxide,

43.668 gms. of phosphorus combine with 56.332 gms. of oxygen

∴ 1 gm " " " " " " " combines with $\frac{56.332}{43.668}$ or 1.29 gms. of

oxygen

In the second oxide,

49.212 gms. of phosphorus combine with 50.788 gms. of oxygen

∴ 1 gm. " " " " " " " combines " $\frac{50.788}{49.212}$ or 1.032 gms of oxygen

In the third oxide,

56.365 gms. of phosphorus combine with 43.635 gms. of oxygen

∴ 1 gm. " " " " " " " combines " $\frac{43.635}{56.365}$ or 0.774 gm. of "

∴ The ratio of the different weights of oxygen that combine with a fixed weight of phosphorus (1 gm.) is 1.29 : 1.032 : 0.774 i.e., 5 : 4 : 3 which is a simple ratio and thus the results are in agreement with the law of multiple proportions.

The same conclusion can be drawn by finding out the ratio of the different weights of phosphorus with a fixed weight of oxygen.

(8) A metal forms two oxides ; on heating 1 gm. of each of the oxides in a current of hydrogen 0.798 gm. and 0.888 gm. of the metal were obtained. Show that the results are in agreement with the law of multiple proportions.

In the first oxide,

(1 - 0.798) or 0.202 gm. of oxygen combines with 0.798 gm. of metal

∴ 1 gm. of oxygen combines with $\frac{0.798}{0.202} = 3.95$ gms. of metal

In the second oxide,

(1 - 0.888) or 0.112 gm. of oxygen combines with 0.888 gm. of metal

∴ 1 gm. of oxygen combines with $\frac{0.888}{0.112} = 7.9$ gms. of metal

The ratio of the different wts of the metal that combine with a fixed weight of oxygen (1 gm.) is 3.95 : 7.9 i.e., 1 : 2 which is a simple ratio. Hence, the results are in agreement with the law of multiple proportions.

(9) A metal 'M' forms two oxides ; 1 gm. of each of the oxides when heated to a constant weight in a current of pure hydrogen gave 0.12585 gm. and 0.2264 gm. of water respectively. Prove that the results illustrate the law of multiple proportions.

1 gm. of the first oxide of M gave 0.12585 gm. of water

Now, since 18 gms. of water contain 16 gms. of oxygen

∴ 0.12585 gm. of water contains $\frac{16 \times 0.12585}{18} = 0.1119$ gm. of oxygen (approx.)

So, 1 gm. of the first oxide contains 0.1119 gm. of oxygen

∴ (1 - 0.1119) or, 0.8881 gm. of the metal.

0.8881 gm. of the metal combines with 0.1119 gm. of oxygen

∴ 1 gm. of the metal combines with $\frac{0.1119}{0.8881} = 0.126$ gm. (approx.)

Again 1 gm. of the second oxide of M gave 0.2264 gm. of water

As above, 0.2264 gm. of water contains $\frac{16 \times 0.2264}{18} = 0.2013$ gm. of oxygen (approx.)

In 1 gm. of the second oxide, metal present = (1 - 0.2013) gm = 0.7987 gm

So, 0.7987 gm. of the metal combines with 0.2013 gm. of oxygen

∴ 1 gm. of the metal combines with $\frac{0.2013}{0.7987} = 0.252$ gm. of oxygen (approx.)

Hence, the ratio of different weights of oxygen that combine with a fixed weight of the metal (1 gm.) in the two oxides is 0.126 : 0.252

or 1 : 2. It is a simple ratio and thus illustrates the law of multiple proportions.

(10) Two oxides of a metal 'M' were separately heated in a current of hydrogen until constant weights were obtained. The water produced in each case was carefully collected and weighed. 2 grams of each of the oxides gave 0.2517 gm. and 0.4528 gms. of water respectively. If the formula for the latter be given as MO, find the formula of the other.

2 gms. of each of the oxides of M gave 0.2517 gm. and 0.4528 gm. of water respectively. \therefore 1 gm. of each of the oxides will give 0.2517/2 gm. and 0.4528/2 gm. or 0.12585 gm. and 0.2264 gm. of water respectively.

Then, according to the previous example (Q. No. 9), 1 gm of the first oxide contains 0.1119 gm of oxygen and 0.8881 gm of the metal.

1 gm of the second oxide contains 0.2013 gm of oxygen and 0.7987 gm of the metal.

Formula of the second oxide = MO (given)

$$\therefore \frac{\text{Number of atoms of M}}{\text{Number of atoms of O}} = \frac{1}{1} = \frac{0.7987/A}{0.2013/16}$$

(A = At. wt of M, 16 = At. wt. of oxygen)

$$\therefore A = 63.49$$

$$\begin{aligned} \text{Now, in the first oxide, } \frac{\text{Number of atoms of M}}{\text{Number of atoms of O}} \\ = \frac{0.8881/63.49}{0.1119/16} = \frac{2}{1} \end{aligned}$$

\therefore The formula of the first oxide is M_2O

On the law of reciprocal proportions—

(11) 2 gms of hydrogen combine with 16 gms of oxygen to form water and 6 gms of carbon to form methane. In carbon dioxide, 12 gms of carbon are combined with 32 gms of oxygen. Show that these figures illustrate the law of reciprocal proportions.

Ratio between the weights of carbon and oxygen that combine with the same weight of hydrogen (2 gms) is 6 : 16. In carbon dioxide, the ratio between the weights of carbon and oxygen which combine with each other is 12 : 32,

The two ratios 6 : 16 and 12 : 32 are simply related to each other as 1 : 1. So the figures illustrate the law of reciprocal proportions.

(12) The results of analysis of three compounds are :

Phosphine (PH_3) contains 91.1% of P and 8.9% of hydrogen ; water contains 88.8% of oxygen and 11.2% of hydrogen and phosphorus trioxide (P_2O_3) contains 56.4% of phosphorus and 43.6% of oxygen. Without the help of atomic weights, show that these results prove the validity of the law of reciprocal proportions.

In phosphine,

8.9 parts by wt. of hydrogen combine with 91.1 parts by wt. of phosphorus,

In water,

11.2 parts by wt. of hydrogen combine with 88.8 parts

by wt. of oxygen
 $\therefore 8.9 \text{ " " " " " " " } \frac{88.8 \times 8.9}{11.2} \text{ or } 70.56$
 parts by wt. of oxygen

\therefore The ratio between the weights of phosphorus and oxygen that combine with a fixed weight of hydrogen (8.9 parts) is $\frac{91.1}{70.56}$

In phosphorus trioxide,

Wt. of phosphorus = 56.4 parts and wt. of oxygen = 43.6 parts

The ratio between the weights of phosphorus and oxygen that combine with each other is $\frac{56.4}{43.6}$

The two ratios are $\frac{91.1}{70.56}$ and $\frac{56.4}{43.6}$ or 1.29 and 1.29. Thus the two wts are simply related as 1 : 1 i.e., they are same. So the results prove the validity of the law of reciprocal proportions.

(13) Carbon dioxide and aluminium carbide contain respectively 27.27% and 25% of carbon. Analysis of aluminium oxide shows that it contains 47% of oxygen. Show that these figures are in agreement with the law of reciprocal proportions.

Carbon dioxide contains 27.27% carbon

and hence (100—27.27) or 72.73% oxygen.

27.27 parts by wt. of carbon combine with 72.73 parts

by wt. of oxygen
 $\therefore 1 \text{ part " " combines " } \frac{72.73}{27.27} = 2.66 \text{ parts by wt. of oxygen}$

Aluminium carbide contains (100—25) or 75% Aluminium
 25 parts by wt. of carbon combine with 75 parts by wt. of aluminium

$\therefore 1 \text{ part " " combines " } \frac{75}{25} = 3 \text{ " " " " " }$

So, the ratio between the weights of oxygen and aluminium that combine with a fixed weight of carbon (1 part) is 2.66 : 3 or 1 : 1.12 ; If the law of reciprocal proportion is applicable, the weights of oxygen and aluminium will be in the same ratio or simple multiples of the weights of the two elements.

Analytical result of aluminium oxide shows that the ratio of the weights of oxygen to aluminium is 47 : (100—47) or 47 : 53 or 1 : 1.12.

So the figures are in agreement with the law of reciprocal proportions.

CHAPTER 3

AVOGADRO'S HYPOTHESIS AND MOLECULAR THEORY

✓ **Adoption of Avogadro's Hypothesis—Concept of molecule:** Dalton's atomic theory states that the elements in general combine in simple proportions by atoms to give rise to the smallest particle or the atom of a compound. Dalton did not think of the existence of the molecule,

Soon after Dalton put forward his atomic theory, Gay Lussac, as a result of a large number of experiments on reactions involving gaseous substances, enunciated the law of gaseous volumes. According to this law, under a given condition of temperature and pressure, elements in the gaseous state unite in simple proportions by volumes. As all gases were found to behave similarly with regard to change of temperature and pressure, it was evident that for a reaction between gases, there must be some simple relation between the number of atoms present in equal volumes of different gases under the identical physical conditions.

In an attempt to correlate Dalton's atomic theory with Gay Lussac's law of gaseous volumes, Berzelius stated that *under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of atoms*. This is commonly known as *Berzelius hypothesis*. But this hypothesis was subsequently found to be untenable as it failed to interpret the experimental results and led to a conclusion which directly contradicted the very basic assumption of Dalton's atomic theory, i.e., indivisibility of an atom.

It has been found experimentally that under the identical conditions of temperature and pressure, 1 vol. of hydrogen and 1 vol. of chlorine interact to produce 2 vols of hydrogen chloride.

Let n be the number of atoms present in unit volume of each of the reacting gases and the product. Then, according to this hypothesis,

$$\begin{aligned} n \text{ atoms of hydrogen} + n \text{ atoms of chlorine} &= 2n \text{ atoms of} \\ &\quad \text{hydrogen chloride} \\ \text{or } 1 \text{ atom of hydrogen} + 1 \text{ atom of chlorine} &= 2 \text{ atoms of hydrogen} \\ &\quad \text{chloride.} \end{aligned}$$

$$\therefore \frac{1}{2} \text{ atom of hydrogen} + \frac{1}{2} \text{ atom of chlorine} = 1 \text{ atom of hydrogen chloride.}$$

So, it leads to accept that 1 atom of hydrogen chloride, is composed of $\frac{1}{2}$ atom of hydrogen and $\frac{1}{2}$ atom of chlorine. In other words, each atom of hydrogen and chlorine requires to be divided to form

an atom of hydrogen chloride. But this is a direct contradiction to Dalton's atomic theory and the division of atoms is in no way acceptable. Hence, Dalton's theory and Gay Lussac's law could not be harmonised by Berzelius hypothesis.

The hypothesis met similar failure when applied to the volumetric composition of steam.

From actual experiments, we know that under the similar physical conditions, 2 vols of hydrogen and 1 vol. oxygen combine chemically to yield 2 vols of steam. Let n stand for the number of atoms present in unit volume of each of the gaseous substances. Now, according to this hypothesis.

$2n$ atoms of hydrogen + n atoms of oxygen = $2n$ atoms of steam
 \therefore 2 atoms of hydrogen + 1 atom of oxygen = 2 atoms of steam
 \therefore 1 atom of hydrogen + $\frac{1}{2}$ atom of oxygen = 1 atom of steam
 \therefore 1 atom of steam contains 1 atom hydrogen and $\frac{1}{2}$ atom of oxygen. That is to say, every atom of oxygen gets divided to form an atom of steam. But this is not possible as according to Dalton, an atom is the smallest conceivable particle and does not undergo sub-division.

This difficulty was overcome by the Italian scientist Avogadro, who for the first time differentiated between the smallest or the ultimate particle of an element and that of a gas. He was the first scientist to imagine the existence of molecules and to propose the molecular theory of matter. According to him, there are two kinds of ultimate particles of matter viz. an atom and a molecule.

Previously, the word atom* has been used indiscriminately to describe the smallest conceivable particle of any substance either an element or a compound.

But Avogadro imposed restriction on the use of the word. According to his suggestions, the term atom should be used for elements only. Moreover, he introduced the term 'molecule' which could be applied for an ultimate particle of both elements and compounds. The distinction between an atom and a molecule will be clearly understood from the following definitions.

An atom is the smallest particle of an element that can take part in a chemical change but generally cannot exist freely as such.

A molecule is the smallest particle of a substance (element or compound) which has free or independent existence and possesses all the characteristic properties the substance.

A molecule of an element is composed of indivisible but like atoms and a molecule of a compound contains fixed number of one



fig. 1(11)—Avogadro

*Dalton used the word 'compound atom' for the smallest particle of a compound.

or more atoms of two or more elements. Thus, a molecule may be divisible into its constituent atoms but an atom is indivisible. According to Avogadro, the ultimate particle of a gas with free existence is not a single atom but a molecule which is composed of more than one atom.

So, it is evident from the concept of molecules that a gas always contains molecules as its ultimate particles and as such the volume of a gas must be related to the number of molecules present in it. In modification of Berzelius' conclusion, Avogadro proposed a new hypothesis which is known as Avogadro's hypothesis.

Avogadro's hypothesis: Under the same conditions of temperature and pressure, equal volumes of all gases (both elementary and compound) contain equal number of molecules.

Thus if n stands for the number of molecules of hydrogen present in 1 litre of the gas under a given condition of temperature and pressure, then according to Avogadro's hypothesis, 1 litre of oxygen, 1 litre of carbon di-oxide or 1 litre of hydrogen chloride will also contain n number of molecules of the respective gaseous substances under the identical physical conditions. It has been illustrated in the following fig. by taking three different gases in three different vessels at a fixed temperature and pressure.

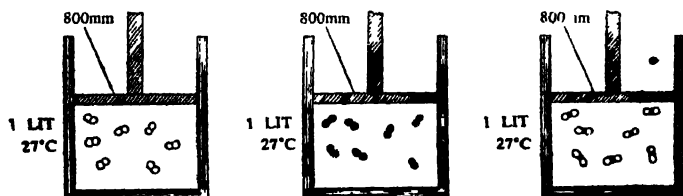


Fig. 1(12) Equal number of molecules of different gases at a fixed temp. and pressure

This hypothesis removed the difficulties of Berzelius' suggestion. In fact, it reconciled the Gay Lussac's law with Dalton's atomic theory.

By actual experiment, we find that under a given condition of temp. and pressure, 1 vol. of hydrogen combines with 1 volume of chlorine to give 2 vols. of hydrogen chloride. According to Avogadro's hypothesis, let ' n ' be the number of molecules present in 1 vol. of each of the gaseous substances.

$\therefore n$ molecules of hydrogen + n molecules of chlorine = $2n$ molecules of hydrogen chloride

$\therefore 1$ molecule of hydrogen + 1 molecule of chlorine = 2 molecules of hydrogen chloride

$\therefore \frac{1}{2}$ molecule of hydrogen + $\frac{1}{2}$ molecule of chlorine = 1 molecule of hydrogen chloride

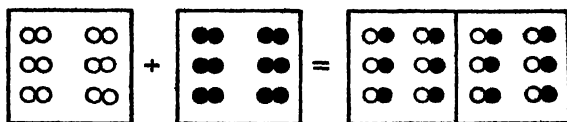
That is to say, 1 molecule of hydrogen chloride must contain $\frac{1}{2}$ molecule of hydrogen and $\frac{1}{2}$ molecule of chlorine. This is in no way

against Dalton's atomic theory. Though the atoms are indivisible, the division of molecules is acceptable. Later, it has been shown that a molecule of hydrogen or that of chlorine consists of two atoms of the respective element.

$\therefore \frac{1}{2}$ molecule of hydrogen (or chlorine) = 1 atom of hydrogen (or chlorine)

This hypothesis tells that during a chemical change, the molecules of the reacting gaseous substances break up into their constituent atoms and the latter are then regrouped into new molecules.

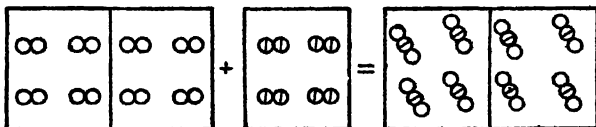
This has been clearly expressed in the following figures.



1 ATOM HYDROGEN = \circ ; 1 ATOM CHLORINE = \bullet ; 1 MOLECULE HYDROGEN = $\circ\circ$;
1 MOLECULE CHLORINE = $\bullet\bullet$; 1 MOLECULE HYDROGEN CHLORIDE = $\circ\bullet$

Fig. 1 (13)

1 volume of hydrogen + 1 volume of chlorine = 2 volumes of hydrogen chloride.



1 ATOM OXYGEN = \bullet , 1 MOLECULE OXYGEN = $\bullet\bullet$, 1 MOLECULE STEAM = $\circ\bullet\bullet$

Fig. 1 (14)

2 volumes of hydrogen + 1 volume of oxygen = 2 volumes of steam
Explanation of Gay Lussac's law of gaseous volumes with the help of Avogadro's hypothesis :

Gay Lussac's law of gaseous volumes follows directly from Avogadro's hypothesis if we consider that when molecules react they do so by simple whole numbers.

Let us suppose that two gases A and B combine chemically and x molecules of A combine with y molecules of B to give a particular compound of A and B. Here x and y are simple whole numbers. Let us further suppose that in accordance with Avogadro's hypothesis, a unit volume in ml. of each of these gases contains n number of molecules at a given temperature and pressure.

So the vols. of the reacting gases are—

$$\text{Vol. of A} = \frac{x}{n} \text{ ml. and vol. of B} = \frac{y}{n} \text{ ml.}$$

It follows, therefore, that the ratio of the volumes in which the gases A and B interact is $\frac{x}{n} : \frac{n}{y} = x : y$.

Since x and y are both small whole numbers, $x : y$ is a simple ratio. Thus the law is derived. ✓

Now, let us consider that C is the gaseous product formed as a result of the reaction between the gases A and B. Here, the number of molecules of C must also be integral as the fractions of molecules cannot exist in the free state. So the volume of gaseous product (or vols. of products) will bear a simple ratio to that of the reacting gases. ✓

Modifications of Dalton's Atomic theory in the light of Avogadro's hypothesis: With the adoption of Avogadro's hypothesis, Dalton's atomic theory has been modified to a great extent. Some of the salient points in this connection are stated below.

(1) Any substance (either an element or a compound) consists of molecules which are the ultimate particles capable of independent existence. The molecules on the other hand are composed of indivisible particles of elements called atoms,

(2) The properties of a substance (elementary or compound) are the properties of its molecules.

The molecules of a particular substance are all alike in respect of properties and mass but the molecules of different substances must possess dissimilar properties and mass.

(3) A molecule of an element contains like atoms but the molecule of a compound is made up of fixed number of atoms which are not all alike.

(4) Atoms only can take part in a chemical change and molecules as they are cannot. At the moment of chemical reaction between two or more substances, the molecules of the reacting substances first split up into their atoms which then combine together in simple ratio to form molecules of the new substance or substances.

Molecular weight: Like the atom of an element, the molecule of an element or a compound is a very small particle with negligible weight. The actual weight of a molecule of hydrogen and that of a molecule of sodium chloride have been calculated and found to be 3.32×10^{-24} gms and 9.71×10^{-23} gms respectively.

As the atomic weights, the molecular weights used in chemical calculations do not signify the actual weights of the molecules. These are also relative weights which are obtained in comparison with the weight of a standard atom. Hence, *the molecular weights are mere numbers and have no unit.*

✓ According to modern standards,

The molecular weight of a substance (either an element or a compound) may be defined as the weight of a molecule of the substance compared with the weight of an atom of hydrogen taken as 1.008 or the weight of an atom of oxygen taken as 16.00 or the weight of an atom of carbon taken as 12.00.

$$\text{Molecular weight} = \frac{\text{Wt. of one molecule of a substance}}{\text{Wt. of one atom of hydrogen (H=1.008)}}$$

or, $\text{Wt. of one atom of oxygen (O=16.00)}$
 or, $\text{Wt. of one atom of carbon (C=12.00)}$ ✓

The molecule of an element is composed of atoms of the same element and the molecule of a compound is formed by the union of atoms of different elements. So from the practical point of view *(the molecular weight may be regarded simply as the sum of the atomic weights of all the atoms present in the molecule.)*

As for example—

Substance ¹	Constituent atoms	Molecular Weight
Hydrogen	$\left. \begin{array}{l} \text{H}_2 \\ \text{N}_2 \\ \text{O}_2 \end{array} \right\}$ A molecule of each of the three substances is di-atomic.	$1 \times 2 = 2$ (actually
Nitrogen		$1.008 \times 2 = 2.016$)
Oxygen		$14.008 \times 2 = 28.016$
Ammonia	NH_3 , a compound consisting of one atom of nitrogen and three atoms of hydrogen.	$16 \times 2 = 32$
Sulphuric acid	H_2SO_4 , a compound containing 2 atoms of hydrogen, 1 atom of sulphur and 4 atoms of oxygen.	$14.008 + 1.008 \times 3 = 17.032$
Cane Sugar	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	$1.008 \times 2 + 32.066 + 4 \times 16$ $= 98.082$
		$12 \times 12 + 1.008 \times 22 + 16 \times 11$ $= 342.176$

The molecular weight of a substance is sometimes referred to as the *formula weight*. Apparently, there is no difference between the terms 'molecular weight' and 'formula weight'. Strictly speaking, molecular weight is applicable to the molecule of a substance. It is now known that there are substances (strong electrolytes) which actually do not exist in the molecular form. They remain as ions even in the solid state. Sodium chloride is a familiar example of this class. X-ray analysis and other experimental results have proved that the salt has no definite entity as a molecule but is composed of Na^+ and Cl^- ions bound together by electrostatic attraction. In such a case, it will be correct to use the term formula weight in place of molecular weight. Of course, the formula weight may be applied to any substance, no matter whether it exists as molecules or ions held together.

Gram-molecular weight or Gram-molecule : A quantity in grams which is numerically equal to the molecular weight of an element or a compound is known as the gram-molecular weight. In other words the molecular weight of any substance (elementary or compound) expressed in grams is referred to as the gram-molecular weight more

frequently as the gram-molecule of the substance. Commonly, this quantity is stated as a mole (sometimes spelled as mol). Thus,

1 gm-molecule of carbon di-oxide	=44 gms of carbon dioxide
1 gm-molecule of water	=18 gms of water
1 gm-molecule of chlorine	=71 gms of chlorine
1 gm-molecule of sulphuric acid	=98 gms of sulphuric acid
3 gm-molecules of sulphuric acid	=3 × 98 gms of sulphuric acid
0.5 gm-molecule of sulphuric acid	=49 gms of sulphuric acid ✓

In the above examples, the atomic weights based on hydrogen scale have been used. (i.e. H=1, Cl=35.5, S=32.00).

Gram-molecular volume or Molar volume :

The volume occupied by 1 gm-molecule of any gaseous substance is known as the gram-molecular volume or simply molar volume. It has been derived from Avogadro's hypothesis that the gram-molecular weight of any gaseous substance or vapour occupies 22.4 litres at N.T.P. So at normal conditions of temperature and pressure, the volume equal to 22.4 litres is the molar volume of all gases.

It is clear from the fig. given below that 32.00 gms of oxygen, or 28 gms of nitrogen, 17 gms of ammonia or 36.5 gms of hydrogen chloride will occupy 22.4 litres at N.T.P.

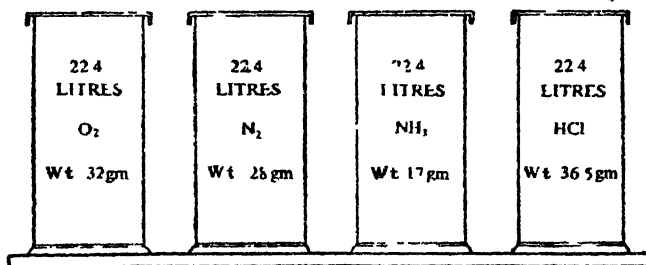


Fig. 1(15) Molar volume

In the light of this discussion, the gram-molecule of a substance may be defined as the weight of the substance in gram which in its gaseous state occupies 22.4 litres at N.T.P.

Applications of Avogadro's hypothesis and its important deductions : In addition to offering a clear explanation of Gay Lussac's law of combining volumes, Avogadro's hypothesis led to the following important deductions and applications.

- (1) The molecules of elementary gases are diatomic.
- (2) The molecular weight of any gaseous (or vaporous) substance is twice its vapour density.

(3) The molar volume or the volume which 1 gm-molecule of any gaseous substance (elementary or compound) occupies is 22.4 litres at N.T.P.

(4) It provides a method of determining the molecular formula of a gaseous substance from its volumetric composition.

(5) It has established methods of determination of atomic weights of elements and molecular weights of gaseous, vaporous or volatile substances.

(1) Molecules of elementary gases are diatomic or atomicity of an elementary gas is 2 :

(A) From actual experiment, it is known that

1 vol. of hydrogen combines with 1 vol. of chlorine to yield
2 vols of hydrogen chloride.

If n be the number of molecules present in unit volume of each of the gaseous substances taking part in the reaction at the experimental conditions of temperature and pressure, we get according to Avogadro's hypothesis,

n molecules of hydrogen + n molecules of chlorine = $2n$ molecules of hydrogen chloride

\therefore 1 molecule of hydrogen + 1 molecule of chlorine = 2 molecules of hydrogen chloride

\therefore $\frac{1}{2}$ molecule of hydrogen + $\frac{1}{2}$ molecule of chlorine = 1 molecule of hydrogen chloride

Now, hydrogen chloride is a compound of hydrogen and chlorine and as per requirement of Dalton's theory, one molecule of hydrogen chloride must contain at least one atom of hydrogen and one atom of chlorine. It is evident that one molecule of hydrogen chloride contains $\frac{1}{2}$ molecule of hydrogen and $\frac{1}{2}$ molecule of chlorine. So each molecule of hydrogen or chlorine must consist of two atoms i.e., a molecule of hydrogen or chlorine is diatomic.

This can further be substantiated by the following reasoning. We know that the number of sodium salts that can be obtained from an acid is a measure of the number of replaceable hydrogen atoms the acid contains. Now, a hydrochloric acid molecule yields one and only one sodium salt (sodium chloride). This indicates that a molecule of the acid contains only one replaceable hydrogen atom. But as stated previously, hydrochloric acid contains $\frac{1}{2}$ molecule of hydrogen.

\therefore $\frac{1}{2}$ molecule of hydrogen = 1 atom of hydrogen.

or, 1 molecule of hydrogen = 2 atoms of hydrogen

\therefore A molecule of hydrogen is diatomic or atomicity of hydrogen is 2.

* Atomicity of an element is the number of atoms present in its single molecule.

(B) From experiment, it is found that 2 vols of hydrogen combine with 1 vol. of oxygen to produce 2 vols of steam.

\therefore $2n$ molecules of hydrogen + n molecules of oxygen = $2n$ molecules of steam (according to Avogadro's hypothesis)

\therefore 2 molecules of hydrogen + 1 molecule of oxygen = 2 molecules of steam

\therefore 1 molecule of hydrogen + $\frac{1}{2}$ molecule of oxygen = 1 molecule of steam

Steam is composed of two elements—hydrogen and oxygen. According to Dalton, an atom is indivisible. So each molecule of steam must contain at least one atom of oxygen which on the other hand must come from $\frac{1}{2}$ molecule of oxygen. Hence a molecule of oxygen must contain 2 atoms of oxygen i.e., the molecular formula of oxygen is O_2 .

Similarly, it can be proved that a molecule of any one of the elementary gases like nitrogen, fluorine etc. is diatomic.

Further evidence in support of the above deduction may be cited. It has been experimentally determined that for a gas with diatomic molecules the ratio $\left(\frac{C_p}{C_v} = \gamma\right)$ of the specific heat at constant pressure (C_p) to the specific heat at constant volume (C_v) is between 1.40 and 1.41. In the case of hydrogen chloride and oxygen γ has been found respectively to be 1.41, 1.40 and 1.40. This remarkable agreement proves beyond doubt the diatomic nature of the molecules of the gases referred to here.

There are some *exceptions* to the above deduction. Inert gases of the atmosphere i.e. helium, argon, neon etc., are elementary gases but they are monatomic. In case of vapours of many metals such as sodium, mercury etc., the smallest conceivable particle or the atom is quite stable and is capable of independent existence. For these elements, the atoms and the molecules are regarded as identical.

(2) Molecular weight of any gaseous substance is twice its vapour density or $M = 2D$, where M = mol. wt. ; D = vap. density.

The vapour density (or relative density) of any gas or vapour is the ratio of the weight of a certain volume of the gas (or vapour) to the weight of the equal volume of hydrogen, both measured under similar conditions of temperature and pressure. Thus—

Vapour density (D) = $\frac{\text{Wt. of } V \text{ volume of any gas}}{\text{Wt. of } V \text{ volume of hydrogen}}$
(under like conditions of temperature and pressure)

If n be the number of molecules present in the given V volume of the gas, then by Avogadro's hypothesis,

$$D = \frac{\text{Wt. of } n \text{ molecules of the gas}}{\text{Wt. of } n \text{ molecules of hydrogen}}$$

$$= \frac{n \times \text{wt. of 1 molecule of the gas}}{n \times \text{wt. of 1 molecule of hydrogen}}$$

$$= \frac{\text{Wt. of 1 molecule of the gas}}{\text{Wt. of 1 molecule of hydrogen}}$$

$$= \frac{\text{Wt. of 1 molecule of the gas}}{2 \times \text{wt. of 1 atom of hydrogen}} \left[\begin{array}{l} \because \text{Hydrogen molecule} \\ \text{is diatomic according} \\ \text{to Avogadro's hypo-} \\ \text{thesis.} \end{array} \right]$$

$$= \frac{1}{2} \text{ Molecular weight of the gas} \\ [\text{assuming atomic wt. of Hydrogen} = 1]$$

$$2 \times D = \text{Molecular weight of the gas}$$

$$\therefore \text{Molecular weight of a gas (M)} = 2 \times \text{Vapour density}$$

$$\text{or } M = 2D.$$

The atomic weight of hydrogen is 1.008 when oxygen (O=16) is considered as the standard. In that case, $M = 2.016 \times D$.

(3) The molar volume of all gases is the same under similar conditions of temperature and pressure and is equal to 22.4 litres at N.T.P.

We know that the gram-molecular weight (or the gm-molecule) of a substance stands for its molecular weight expressed in grams. Now,

(a) At wt. of hydrogen = 1

\therefore Mol wt. of hydrogen = 2 (\because hydrogen molecule is diatomic)

\therefore 1 gm-molecule of hydrogen = 2 gms. of hydrogen.

If w be the actual weight of 1 atom of hydrogen in gm, then the actual wt. of 1 molecule of hydrogen = $2w$ gms

\therefore Number of hydrogen molecules present in 1 gm-molecule

$$\text{of it} = \frac{2 \text{ gms}}{2w \text{ gms}} = \frac{1}{w}$$

(b) 1 gm molecule of nitrogen = 28 gms of nitrogen. In other words, 1 molecule of nitrogen is 28 times heavier than 1 atom of hydrogen.

\therefore Actual weight of 1 molecule of nitrogen = $28w$ gms

\therefore Number of nitrogen molecules present in 1 gm-molecule

$$\text{of nitrogen} = \frac{28 \text{ gms}}{28w \text{ gms}} = \frac{1}{w}$$

(c) Vapour density of ammonia = 8.5 (found by experiment)

\therefore Molecular weight of ammonia = $2 \times 8.5 = 17$

and 1 gm-molecule of ammonia = 17 gms. of ammonia

So 1 molecule of ammonia is 17 times heavier than 1 atom of hydrogen.

\therefore Wt. of 1 molecule of ammonia = $17w$ gms.

∴ Number of molecules of ammonia present in its 1 gm-molecule

$$= \frac{17 \text{ gms}}{17w \text{ gms}} = \frac{1}{w}$$

(d) Vapour density of sulphur dioxide = 32
(determined experimentally)

∴ Mol. wt. of sulphur dioxide = $2 \times 32 = 64$ and 1 gm-molecule of sulphur dioxide = 64 gms of sulphur dioxide. In other words, 1 molecule of sulphur dioxide is 64 times heavier than 1 atom of hydrogen.

∴ Wt. of 1 molecule of sulphur dioxide = $64w$

∴ Number of molecules of sulphur dioxide in 1 gm-molecule

$$= \frac{64 \text{ gms}}{64w \text{ gms}} = \frac{1}{w}$$

Thus it can be shown that for any gas (or vapour) the number of molecules present in its 1 gm-molecule is the same and is equal to $\frac{1}{w}$. Now from Avogadro's hypothesis, it can reasonably be concluded that the same number of molecules of different gases will occupy the same volume at a given condition of temp. and pressure. In other words, the gm-molecule of all gases will occupy the same volume under the same conditions of temperature and pressure.

Let us assume the vapour density of a gas (or vapour) = D

$$\begin{aligned} \therefore \text{By definition, } D &= \frac{\text{Wt. of 1 litre of the gas at N.T.P.}}{\text{Wt. of 1 litre of the hydrogen at N.T.P.}} \\ &= \frac{\text{Wt. of 1 litre of the gas at N.T.P.}}{0.089 \text{ gm}} \end{aligned}$$

(It is known from actual experiment that weight of 1 litre of hydrogen at N.T.P. is 0.089 gm)

∴ At N.T.P. weight of 1 litre of any gas = $(D \times 0.089) \text{ gms.}$

But according to Avogadro's hypothesis $M = 2D$

where M = molecular weight.

$$\therefore D = \frac{M}{2}$$

So under normal conditions of temperature and pressure,

The weight of 1 litre of a gas = $\left(\frac{M}{2} \times 0.089\right) \text{ gm}$

i.e. At N.T.P., the vol occupied by $\left(\frac{M}{2} \times 0.089\right) \text{ gm}$ of a gas = 1 litre.

\therefore At N.T.P. the volume occupied by M gms or 1 gm-molecule of any gas = $\frac{2 \times M}{M \times 0.089} = \frac{2}{0.089}$ litres = 22.4 litres

Based on Avogadro's hypothesis, the molecular weight may be defined as follows :

The molecular weight of a substance is a number which when expressed in grams would be equal to the weight of 22.4 litres at N.T.P. of the substance in its gaseous or vaporous state.

N.T.P. is the abbreviation of normal temp. and pressure. Normal temp. denotes 0°C or 373°A . The pressure of the atmosphere which is equal to that of a column of mercury 76 cm or 760 mm high is referred to as normal pressure.

(4) **Determination of molecular formula of a gaseous compound from its volumetric composition:** Avogadro's hypothesis helps us in determining the molecular formula of a gaseous compound from its volumetric composition and density.

Illustrations—(A) Molecular formula of hydrogen chloride: By actual experiment, it has been found that 1 volume of hydrogen combines with 1 volume of chlorine to produce 2 volumes of hydrogen chloride, all volumes being measured under the same conditions of temperature and pressure.

Let n stand for the number of molecules present in unit volume of any of the gases. Then from Avogadro's hypothesis, it follows that

n molecules of hydrogen + n molecules of chlorine = $2n$ molecules of hydrogen chloride

\therefore 2 atoms of hydrogen + 2 atoms of chlorine = 2 molecules of hydrogen chloride

(\therefore According to Avogadro's hypothesis, both hydrogen molecule and chlorine molecule are diatomic).

1 atom of hydrogen + 1 atom of chlorine = 1 molecule of hydrogen chloride.

\therefore 1 molecule of hydrogen chloride contains 1 atom of hydrogen and 1 atom of chlorine i.e., the simplest formula for hydrogen chloride is HCl and the molecular formula of it is $(\text{HCl})_x$ when x is a positive integer

\therefore Molecular weight = $(1 + 35.5)$

As found experimentally, the vapour density of hydrogen chloride is 18.25.

\therefore Its molecular weight = $2 \times 18.25 = 36.50$

$\therefore (36.5)_x = 36.5$ or, $x = 1$

\therefore Molecular formula of hydrogen chloride = HCl.

(B) *Molecular formula of ammonia :*

It is known from experimental results that under given conditions of temperature and pressure, 1 volume of nitrogen chemically combines with 3 volumes of hydrogen to form 2 volumes of ammonia.

\therefore 1 vol. of nitrogen + 3 vols. of hydrogen = 2 vols. of ammonia

\therefore n molecules of nitrogen + $3n$ molecules of hydrogen = $2n$ molecules of ammonia
(According to Avogadro's hypothesis)

\therefore 1 molecule „ „ + 3 molecules of hydrogen = 2 molecules of ammonia

\therefore $\frac{1}{2}$ „ „ „ + $\frac{3}{2}$ „ „ of hydrogen = 1 molecule of ammonia

\therefore 1 atom of nitrogen + 3 atoms of hydrogen = 1 molecule of ammonia

(\because Both nitrogen and hydrogen are diatomic)

i.e. 1 atom of nitrogen and 3 atoms of hydrogen are present in 1 molecule of ammonia.

\therefore The simplest formula of ammonia is NH_3 . This formula for ammonia finds experimental supports from its vapour density measurement.

Let the molecular formula of ammonia is $(\text{NH}_3)_x$ where x is a simple whole number.

\therefore Molecular wt. of ammonia = $(14 + 3)x$

The vapour density of it is found to be 8.5

\therefore Its molecular weight = $2 \times 8.5 = 17$

\therefore $(14 + 3)x = 17$ or, $x = 1$

So the molecular formula of ammonia = NH_3

(C) *Molecular formula of carbon dioxide :*

It has been proved experimentally that 1 volume of carbon dioxide contains 1 volume of oxygen. Let us assume that the volumes of the two gases are measured under identical conditions of temperature and pressure and n stands for the number of molecules of carbon dioxide in unit volume at the experimental conditions.

As deduced from Avogadro's hypothesis, n molecules of carbon dioxide contain n molecules of oxygen.

\therefore 1 molecule of carbon dioxide contains 1 molecule of oxygen

\therefore 1 „ „ „ „ „ 2 atoms of oxygen
(\because atomicity of oxygen is 2)

\therefore Molecular formula of carbon dioxide is C_xO_2

(where x represents the number of atoms of carbon in 1 molecule of carbon dioxide.)

Again, it is known from experiment that the vapour density of carbon dioxide is 22.

\therefore its molecular weight $= 22 \times 2 = 44$.

$$\therefore C_xO_y = 44 \quad \text{or} \quad (12x + 2 \times 16) = 44 \quad \text{or} \quad x = 1$$

\therefore Molecular formula of carbon dioxide = CO_2

(D) ~~Molecular formula of nitrous oxide :~~

From experimental results, we know that nitrous oxide contains its own volume of nitrogen.

\therefore 1 volume of nitrous oxide contains 1 volume of nitrogen, volumes of the two gases being measured at the same temperature and pressure. Let us assume that at a given temperature and pressure, 1 vol. of nitrous oxide contains n number of molecules.

$\therefore n$ molecules of nitrous oxide contain n molecules of nitrogen
(Avogadro's hypothesis)

\therefore 1 molecule of nitrous oxide contains 1 molecule of nitrogen

∴ 1 " " " " 2 atoms of nitrogen
(deduction from Avogadro's hypothesis)

Hence, its formula is N_2O_x (where x stands for the number of oxygen atoms present in 1 molecule of nitrous oxide).

\therefore Molecular weight of nitrous oxide $= 2 \times 14 + 16x$

Vapour density of nitrous oxide has been found to be 22 by actual experiment.

\therefore Its molecular weight $= 2 \times 22 - 44$ ($\because M = 2D$)

$$\therefore 2 \times 14 + 16x = 44 \quad \text{or, } x = 1$$

\therefore Molecular formula of nitrous oxide N_2O .

(5) Determination of atomic weight of an element - Cannizzaro's method :

By applying a basic assumption of Dalton's atomic theory and an important deduction of Avogadro's hypothesis, Cannizzaro devised a method of determining the atomic weights of elements.

Principle : Atoms are indivisible. Under no circumstances, the molecule of any compound can contain less than one atom of any of its constituent elements. So, the smallest weight of any particular element present in the molecular weights of its different compounds may be taken to be the atomic weight of the element.

Procedure : The process involves the following steps.

(a) Selection of a large number of compounds (of the element) which are either volatile or can be gasified without decomposition.

(b) Experimental determination of the vapour densities of the selected compounds.

(c) Calculation of the molecular weights from the relation,
 $M = 2 \times V.D.$

(d) Analysis of the compounds to determine the actual weight of the element present in each compound.

(e) Finding out the smallest weight of the element in the molecular wts (or gm-molecular weights) of the compounds.

It is probable that in a large number of compounds, there must be at least one which will contain a single atom of the particular element. So the smallest or the least weight* will reasonably represent the atomic weight of the element.

Illustration : Atomic weight of oxygen.

Oxygen-compound	Vapour density $D_H = 1$	Molecular weight $(2 \times V.D.)$	% of Oxygen	Wt. of oxygen (in gm) in 1 gm.-molecule
Water vapour	9	18	88.9	$\frac{88.9 \times 18}{100} \approx 16.0$
Carbon monoxide	14	28	57.18	$\frac{16}{16 \times 1}$
Carbon dioxide	22	44	72.73	$\frac{32}{16 \times 2}$
Sulphur dioxide	32	64	50	$\frac{32}{16 \times 2}$
Sulphur trioxide	40	80	60	$\frac{48}{16 \times 3}$
Nitric oxide	15	30	53.33	$\frac{16}{16 \times 1}$

So the smallest weight (better highest common factor of the weights) of oxygen present per gm-molecule of its different compounds is 16 and hence the atomic weight of oxygen may be taken as 16.00.

Limitations of Cannizzaro's method : (1) The method is very laborious and time consuming. (2) This method can be applied only in the case of an element which can form a large number of volatile compounds. (3) The method is based on the belief that out of a large number of compounds of an element, at least one compound containing a single atom of the element will be available. But this may not be true in all cases. (4) At. wt. determined by this method is not always free from error.

* In fact, the smallest weight thus determined may not always be the atomic weight. Atomic weight may best be represented by the highest common factor (H.C.F.) of the different weights of the same element found in 1 gm-molecular weights of its various compounds.

If the atomicity (i.e. number of atoms present in the single molecule) of a gaseous element is known, its atomic weight can be found out from the following relation :

$$\text{Atomic weight} = \frac{\text{Molecular weight}}{\text{Atomicity}}.$$

The vapour density ($H=1$) is determined experimentally. By applying the relation, $2 \times \text{vapour density} = \text{Molecular weight}$, the atomic weight can be known.

Avogadro's Number : The values of the atomic weights and molecular weights as stated earlier are proportional to the actual weights of the atoms and molecules respectively. So it is evident that 1 gm-atom or 1 gm-molecule of a substance should always contain a definite, constant number of individual atoms or molecules.

Further, it has been deduced from the Avogadro's hypothesis that the volume occupied by 1 gm-molecule of any gas is same under the identical conditions of temperature and pressure. Alternatively, it follows that 1 gm-molecule of different gases occupying the same volume will contain the same and constant number of molecules. This constant number of molecules is known as the Avogadro's Number.

Definition of Avogadro's Number : Avogadro's number is usually defined as the number of molecules present in 1 gm-molecule of a substance (an element or a compound). It is denoted by N and its accepted value is 6.023×10^{23} (roughly 6.0×10^{23}).

Avogadro's number which is independent of the pressure and temperature is also equal to the number of atoms present in 1 gm-atom of an element.

Thus 1 gm-molecule or 32 gms of oxygen, 44 gms of carbon dioxide, 30 gms of nitric oxide will contain 6.023×10^{23} molecules of the respective element and the compounds. Similarly, the same number of sodium atoms will be present in 1 gm-atom or 22.998 gms. of sodium.

Absolute weight of a single molecule or an atom : As stated earlier, the actual weight of an atom or a molecule of any substance is too small to be determined by direct weighing. But it has now been found possible to find out the actual weight a single atom or a molecule of any species by dividing the gm-atomic weight or gm-molecular weight by the Avogadro's number. The process of calculation is illustrated below.

$$\begin{aligned} \text{Molecular weight of oxygen is } 32 ; 1 \text{ gm-molecule of} \\ \text{oxygen} = 32 \text{ gms of oxygen} \\ \text{Number of molecules present in 32 gms of oxygen} = N \\ = 6.023 \times 10^{23} \end{aligned}$$

Now, actual weight of 6.023×10^{23} molecules of oxygen = 32 gms

\therefore " " " " 1 molecule " " = $\frac{32}{6.023 \times 10^{23}}$
or 5.81×10^{-23} gms.

Or " " " " 1 atom of oxygen = $\frac{5.81 \times 10^{-23}}{2}$ gm
(\because oxygen molecule is diatomic)

Again, 1 gm-molecule of hydrogen = 2.016 gms of hydrogen
(0=16)

The number of molecules of hydrogen present in this quantity will be equal to N or 6.023×10^{23} .

Now 6.023×10^{23} molecules of hydrogen actually weigh 2.016 gms

\therefore 1 molecule " " " " = $\frac{2.016}{6.023 \times 10^{23}}$ gm

and 1 atom " " " " = $\frac{2.016}{2 \times 6.023 \times 10^{23}}$ gm

(\because Hydrogen molecule is diatomic)
= 0.1673×10^{-23} gm = w gm (say)

The actual or absolute weights of atoms of other elements can be known from the relation.

$A = a \times w$; Where A = actual weight of an atom of a particular element

a = atomic weight of the element

w = actual weight of a hydrogen atom

Thus, the weight of one carbon atom = $12.0 \times 0.1673 \times 10^{-23}$ gm.

Summary of the importance of Avogadro's hypothesis in chemistry: Avogadro's hypothesis plays a very important role in chemistry. Although the hypothesis has not been proved by direct experiments, the deductions made from it have not yet been found to deviate from the experimental results. This hypothesis is now so universally accepted that it is regarded as one of the established laws in chemistry.

This hypothesis first introduced the concept of molecules and made a clear distinction between two kinds of ultimate particles of matter viz. atoms and molecules. It has offered an explanation to the Gay Lussac's law of gaseous volumes. In short, it can reasonably be concluded that Avogadro's hypothesis has placed Dalton's atomic theory on firm footing and greatly extended its usefulness. Moreover, the hypothesis is useful—(a) in determining the atomicity of elementary gases (b) in deducing the relationship, $M = 2V.D$ (where M = molecular wt. and V.D = vapour density). (c) in deducing that the volume of a gram-molecule of any gas is 22.4 litres at N.T.P.

This hypothesis has provided a method of determination of the molecular formula of a gaseous substance from its volumetric composition and established a method of finding out the atomic weights of elements.

Numerical problems

1. (a) 10 c.c. of hydrogen contains 2000 molecules of hydrogen at certain pressure and temperature. Calculate the number of molecules of oxygen whose volume is 150 c.c. at the same temperature and pressure.

(b) The weights of equal volumes of a gas and hydrogen are 28.57 gms and 0.89 gm respectively under the same conditions of temperature and pressure. Find out the molecular weight of the gas.

(c) The density of a gaseous element is 5 times that of oxygen under similar conditions. If the molecule of the element is triatomic, what will be its atomic weight? [W. B. H. S. 1980]

(a) According to Avogadro's hypothesis, at the same temperature and pressure, 10 c.c. of oxygen will contain the same number of molecules as hydrogen i.e. 2000 molecules.

$$\therefore 150 \text{ c.c. of oxygen will contain } \frac{2000 \times 150}{10}$$

or 30,000 molecules

(b) According to the question, vapour density of the gas

$$\frac{28.57}{0.89} = 32.1,$$

By applying the relation $M = 2D$, the molecular weight of the gas $= 2 \times 32.1 = 64.2$

(c) The vapour density of oxygen ($H=1$) = 16 and according to the question, the vapour density of the gaseous element = $5 \times 16 = 80$ and its molecular weight = $2 \times 80 = 160$ (Avogadro's hypothesis).

As the molecule of the element is triatomic, so its

$$\text{atomic weight} = \frac{\text{molecular weight}}{\text{at. molec.}} = \frac{160}{3} = 53.33$$

2. (a) The molecular weight of a gaseous substance is 200. What is the volume of 5 gms of the substance at N.T.P.?

(b) One litre of a gas at N.T.P. weighs 1.904 gms. Find the molecular weight of the gas.

(a) The molecular weight of the substance = 200

$$\therefore 1 \text{ gram-molecule of the substance} = 200 \text{ gms.}$$

Volume of 1 gm-molecule or 200 gms of the substance at N.T.P is 22.4 litres (Avogadro's hypothesis)

$$\therefore \text{Vol of 5 gms of the substance at N. T. P} = \frac{22.4 \times 5}{200} \\ = 0.56 \text{ litre or 560 ml.}$$

$$\begin{aligned} \text{(b) At N.T.P, the weight of 1 litre of the gas} &= 1.964 \text{ gms} \\ \therefore \text{ " " " " " 22.4 litres " " } &= 1.964 \times 22.4 \\ &= 43.99 \text{ gms} \end{aligned}$$

$$\therefore \text{Molecular weight of the gas} = 43.99.$$

3. (a) Pure hydrogen sulphide is stored in a tank of 100 litres at 0°C and a pressure of 760 mm. Calculate the weight of the gas in grams.

(b) Find out the ratio of weights of equal volumes of carbon dioxide and sulphur dioxide both of which are at the same temperature and pressure.

(a) Gram-molecule of hydrogen sulphide (H_2S) = 34 gms.

As per question, the gas is under N.T.P.

At N.T.P 22.4 litres of hydrogen sulphide weigh 34 gms

$$\therefore \begin{array}{ccccccc} \text{"} & \text{"} & \text{100} & \text{"} & \text{"} & \text{"} & \text{"} \\ & & & & & & \frac{34 \times 100}{22.4} \\ & & & & & & = 151.78 \text{ gms} \end{array}$$

(b) The molecular weight of CO_2 = 44 \therefore 1 gm-molecule of CO_2 = 44 gms of CO_2

At N. T. P, the volume occupied by 44 gms of CO_2 = 22.4 litres

The molecular weight of SO_2 = 64

\therefore 1 gm-molecule of SO_2 = 64 gms of SO_2

At N. T. P, the vol. occupied by 64 gms of SO_2 = 22.4 litres

\therefore The weights of equal volumes (22.4 litres) CO_2 and SO_2 at the same temp. and pressure (N. T. P.) are 44 and 64 gms respectively.

\therefore The weight ratio = 44 : 64 or 11 : 16

4. (a) Calculate the number of molecules in a drop of water weighing 0.04 gm. How many atoms of hydrogen and oxygen are present in the same quantity of water?

(b) Assuming the density of water to be 1 g/cc., find the volume occupied by one molecule of water.

(a) 1 gram-molecule of water = 18 gms of water.

18 gms of water contain 6.023×10^{23} molecules (Avogadro's Number)

$$\therefore 0.04 \text{ gm ,, contains } \frac{6.023 \times 10^{23} \times 0.04}{18} = 1.338 \times 10^{21}$$

molecules

1 molecule of H_2O contains two atoms of hydrogen and 1 atom of oxygen.

So, number of atoms of hydrogen = number of molecules of water $\times 2 = 1.338 \times 10^{21} \times 2 = 2.676 \times 10^{21}$

and number of atoms of oxygen = number of molecules of water $= 1.338 \times 10^{21}$

(b) Molecular weight of water 18 and according to the question vol of 18 gms of water = 18 ml and the number of molecules in 18 gms of water $= 6.023 \times 10^{23}$

$\therefore 6.023 \times 10^{23}$ molecules of water occupy 18 ml

$\therefore 1$ " " " $\frac{18}{6.023 \times 10^{23}}$
or 2.99×10^{-23} ml.

(5) (a) What is the volume at N.T.P. of 0.25 gram-atom of chlorine gas?

(b) How many gram-atoms are present in 1.1495 gms of sodium? (At. wt of Na = 22.99)

(a) At N.T.P. 1 gm-molecule of chlorine occupies 22.4 litres

\therefore " " 1 gm-atom " " " $\frac{22.4}{2} = 11.2$ litres
(\because chlorine is diatomic)

\therefore " " 0.25 " " " " 11.2×0.25
 $= 2.8$ litres

(b) The atomic weight of Na = 22.99

\therefore One gram-atom of Na = 22.99 gms of Na

Now, 22.99 gms of Na correspond to 1 gm-atom

$\therefore 1.1495$ " " " $\frac{1.1495}{22.99}$ gram-atoms.
 $= 0.05$ gm atom.

(6) Find out the amount of sulphuric acid that will contain an equal number of molecules as present in 15.75 gms of nitric acid.

1 gm-molecule of nitric acid = 63 gms of nitric acid

\therefore 63 gms of nitric acid contain 6.023×10^{23} molecules

$\therefore 15.75$ " " " " $\frac{6.023 \times 10^{23} \times 15.75}{63}$
 $= 1.50575 \times 10^{23}$ molecules

Again, 1 gm-molecule of sulphuric acid = 98 gms of the acid

Then, 6.023×10^{23} molecules are present in 98 gms of the acid

$\therefore 1.50575 \times 10^{23}$ " " " " $\frac{98 \times 1.50575 \times 10^{23}}{6.023 \times 10^{23}}$
 $= 24.5$ gms. of acid

(7) 250 c.c. of a gas at N. T. P. weigh 0.7524 gm :

What is the exact weight of one molecule of the gas ?

250 c.c. of the gas at N. T. P. weigh 0.7924 gm

$$\therefore 22400 \text{ c.c. of } ,, ,, ,, ,, \quad \frac{0.7924 \times 22400}{250} = 70.999 \text{ gms.}$$

\therefore Gram-molecule of the gas = 70.999 gms.

Number of molecules present in 70.999 gms = 6.023×10^{23}

Now, 6.023×10^{23} molecules weigh 70.999 gms

$$\therefore 1 \text{ molecule weighs } \frac{70.999}{6.023 \times 10^{23}} \text{ gm} \\ = 11.78 \times 10^{-23} \text{ gm.}$$

(8) In 93.0 gm of phosphorus calculate :

(a) the number of gm-atoms of the element

(b) the number of moles, if a molecule of phosphorus has the formula P_4 .

(c) The number of atoms of phosphorus

(d) the number of molecules

(a) Atomic weight of phosphorus = 31

$$\therefore \text{Number of gm-atoms} = \frac{93}{31} = 3$$

(b) 1 mole of $P_4 = 4 \times 31 \text{ gms} = 124 \text{ gms.}$ of it

$$\therefore \text{Number of moles of } P_4 = \frac{93}{124} = 0.75$$

(c) Number of atoms = gram-atom $\times N$ ($N = \text{Avogadro's number}$)
 $= 3 \times 6.02 \times 10^{23} = 1.806 \times 10^{24}$

(d) Number of molecules = Number of moles $\times N$
 $= 0.75 \times 6.02 \times 10^{23} = 4.515 \times 10^{23}$

(9) Equal masses of two gases A and B are kept in two separate vessels under same temperature and pressure. If the ratio of molecular weights of A and B be 2 : 3. Find the ratio of the volumes of the two vessels. [W. B. H. S. 1982]

Let the molecular weights of two gases A and B are M_1 and M_2 respectively and the weight of each of the gases = W gms.

$$\text{Now, } \frac{M_1}{M_2} = \frac{2}{3} \text{ or } M_2 = \frac{3}{2} M_1$$

Volume occupied by M_1 gm of A at N T P. = 22.4 litres

$$\therefore ,, ,, ,, W ,, ,, \quad \frac{22.4 \times W}{M_1} \text{ litres}$$

Again, volume occupied by M_2 gms of B of N.T.P. = 22.4 litres

$$\therefore \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad W \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad = \frac{22.4 \times W}{M_2} \text{ litres}$$

$$= \frac{22.4 \times W \times 2}{3M_1} \text{ litres}$$

\therefore Ratio of the vols of A and B of equal mases

$$= \frac{22.4 \times W}{M_1} : \frac{22.4 \times W \times 2}{3M_1} = 1 : \frac{2}{3} = 3 : 2$$

(10) From 200 mg of CO_2 , 10^{21} molecules are removed. How many moles of CO_2 are left? (Avogadro no = 6.0×10^{23})

Mol. wt. of $\text{CO}_2 = 44$

\therefore 44 gms of $\text{CO}_2 = 1$ mole of CO_2

\therefore 200 mg or 0.2 gm of $\text{CO}_2 = \frac{0.2}{44}$ mole of CO_2

Now, 6×10^{23} molecules of $\text{CO}_2 \equiv 1$ mole of CO_2

\therefore 10^{21} ,, ,, $\equiv \frac{10^{21}}{6 \times 10^{23}}$ or $\frac{1}{600}$ mole of CO_2

SO, the number of moles of CO_2 left = $\left(\frac{0.2}{44} - \frac{1}{600} \right)$ moles

$$= \frac{19}{6600} \text{ or } 0.00287 \text{ moles}$$

N. B. In the following examples, the relation, $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

(the general gas equation obtained by combining Boyle's law and Charles' law) has been applied. This has been thoroughly discussed in chapter 8.

(11) Find out the weight of 1.40 litres of oxygen measured at 0°C and under a pressure of 10 mm and also determine the number of molecules present in it.

Let V_1 be the volume of oxygen at N. T. P. According to the general gas equation,

$$\frac{760 \times V_1}{273} = \frac{10 \times 1.40}{273} \text{ or } V_1 = \frac{10 \times 1.40}{760} \text{ or } \frac{0.7}{38} \text{ litre}$$

Oxygen molecule is diatomic and its gram-molecule is 2×16 or 32 gms.

According to Avogadro's hypothesis

22.4 litres of oxygen at N.T.P. weigh 32 gms

$$\therefore \quad \frac{0.7}{38} \text{ litre of ,, ,, ,, weighs } \frac{32 \times 0.7}{22.4 \times 38} = \frac{1}{38} \text{ gm}$$

$$= 0.0263 \text{ gm.}$$

At N.T.P. 22.4 litres of oxygen contain 6.023×10^{23} molecules

$$\therefore \quad \frac{0.7}{38} \quad \text{,,} \quad \text{,,} \quad \text{contains} \quad \frac{6.023 \times 10^{23} \times 0.7}{22.4 \times 38} = 5 \times 10^{20} \text{ molecules}$$

(12) The volume of 0.393 gm of a certain gas at 27°C and 7.0 mm. pressure is 222.7 c.c. Find the vapour density and molecular weight of the gas.

Let V_1 be the volume of the gas at N.T.P.

$$\frac{760 \times V_1}{273} = \frac{750 \times 222.7}{273 + 27} \quad \text{or} \quad V_1 = \frac{750 \times 222.7 \times 273}{760 \times 300} \quad \text{or} \quad 199.99 \text{ c.c.}$$

$$\text{At N.T.P. the wt. of 1 c.c. of the gas} = \frac{0.393}{199.99} = 0.00196 \text{ gm.}$$

We know that wt. of 1 c.c. of hydrogen at N.T.P. is 0.000089 gm

$$\therefore \text{ Vapour density of the gas} = \frac{0.00196}{0.000089} = 22.02$$

$$\text{Again, molecular weight} = 2 \times \text{vapour density} = 2 \times 22.02 = 44.04$$

(13) A gas mixture containing 80% CO and 20% CO_2 by volume exists at 27°C and 750 mm pressure. How many grams of carbon dioxide are present in 1.52 litres of this gas mixture?

(W. B. H. S. 1978)

Let V_1 be the volume of the gas mixture at N. T. P.

$$\text{Then, from the equation } \left(\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \right)$$

$$\frac{760 \times V_1}{273} = \frac{750 \times 1.52}{273 + 27} \quad \text{Or} \quad V_1 = \frac{750 \times 1.52 \times 273}{760 \times 300} \quad \text{or} \quad 1.365 \text{ litres}$$

As the mixture contains 20% CO_2 by vol,

$$\text{Vol. of } \text{CO}_2 \text{ in 1.365 litres} = \frac{1.365}{5} = 0.273 \text{ litre. According to}$$

Avogadro's hypothesis,

22.4 litres of CO_2 contain 44 gms of CO_2

$$\therefore 0.273 \text{ litre ,, ,, contains } \frac{44 \times 0.273}{22.4} \quad \text{or} \quad 0.536 \text{ gm of } \text{CO}_2$$

CHAPTER 4

SYMBOL, FORMULA, VALENCY AND EQUATION

In order to simplify the study of chemistry, the chemists in the present days have accepted a universal system of using abbreviations or symbolisations to express all chemical changes.

Alchemists at the Middle Age used different mysterious drawings and signs for the names of the substances known to them. The ancient Greek and Hindu astronomers represented some of the metals by the symbols which were the emblems for various heavenly bodies. Thus—

Sun Moon Mars Venus Saturn Jupiter Mercury



Gold Silver Iron Copper Lead Tin Mercury

Fig. 1(16) Ancient symbols of metals.

Dalton however made an attempt to represent elements and compounds through symbols. But the symbols or notations used by him were of very complicated nature and were ultimately abandoned. In fact, the present system of using chemical symbols for elements was introduced by Berzelius in 1811.

Symbol: A symbol is the abbreviated notation used for the full name of an element.

Generally, the initial letter of the English name of an element stands for its symbol. The letter used for this purpose must always be capital. Thus, the symbol of hydrogen is H, that of oxygen is O and of carbon is C.

When the English names of two or more elements begin with the same letter, the initial letter represents only one of them and each of the rest is denoted by two letters where the same initial capital letter is followed a small letter distinctly heard in pronouncing the name of the element. Symbols of some elements of this type are given in the table in the next page.

Element	Symbol	Element	Symbol
Boron	B	Carbon	C
Barium	Ba	Calcium	Ca
Bismuth	Bi	Cadmium	Cd
Bromine	Br	Chlorine	Cl
Beryllium	Be	Chromium	Cr

Sometimes, the letter or the pair of letters used as the symbol is similarly taken from the Latin (or Greek, German etc.) name of the element.

In the following table, the symbols of some elements derived from their Latin (or German) names have been shown.

English name	Latin name	Symbol
Sodium	Natrium	Na
Potassium	Kalium	K
Copper	Cuprum	Cu
Silver	Argentum	Ag
Gold	Aurum	Au
Mercury	Hydrargyrum	Hg
Iron	Ferrum	Fe
Lead	Plumbum	Pb
Tungsten	Wolfram (German name)	W

Full meaning of a symbol : A symbol conveys information both qualitative and quantitative.

Qualitatively, it denotes the full name of the element.

Quantitatively, it stands for (a) one atom of the element.

(b) a quantity corresponding to the atomic weight of the element.

Examples : The symbol 'O' represents the name oxygen, one atom of oxygen and 16 parts by weight of oxygen.

Mg not only stands for magnesium, but also for one atom of magnesium. Moreover, it represents 24 parts by weight of magnesium.

It is to be remembered that if the weight is expressed in grams, a symbol will represent one gm-atom of the element and stands for the number of atoms equal to the Avogadro's number.

Thus in the light of foregoing discussions, a symbol may be defined as—

The first letter alone or along with a distinctly pronounced second letter of the English, Latin or Greek name of the element representing the full name, one atom and atomic weight of the element is called the symbol.

If it is required to denote a number of similar atoms, the required number is placed to the immediate left of the symbol. Thus 2H, 2N represent two atoms of hydrogen and two atoms of nitrogen respectively. A completely different meaning is expressed

when a numeral is placed just below and after the symbol of an element. H_2 and N_2 indicate respectively one molecule of hydrogen and one molecule of nitrogen. Thus, the number on the right of the symbol stands for atomicity or the atoms present per molecule of the element. Three atoms of oxygen are contained in a molecule of ozone, and its molecule is written as O_3 . It is to be remembered that $2H$ represents two separate hydrogen atoms (not united together) while H_2 represents a hydrogen molecule in which the atoms are combined chemically. ✕

✓ **Formula (or molecular formula):** A formula is the symbolic representation of the composition of the molecule of a substance both elementary and compound. A formula is also referred to as the molecular formula as it stands for a discrete molecule.

The formula of an element is denoted by its symbol with a numerical subscript (indicating atomicity) below the right hand side. Thus, the formulae for hydrogen, oxygen, nitrogen and chlorine are H_2 , O_2 , N_2 and Cl_2 respectively (each of the elements is diatomic).

The triatomic molecule of ozone and tetratomic molecule of phosphorus are formulated respectively as O_3 and P_4 . The molecules of the metals like sodium, zinc and mercury are monatomic in vaporous state and are represented by their symbols i.e. by Na , Zn , Hg respectively.

The atoms of the inert gases such as helium, neon, argon etc. exist in the free state. So in the cases of these elements, their symbols stand for their formulae.

A molecule of a compound contains atoms of two or more elements in a particular ratio. In building up the formulae of compounds, the number of atoms of each of the elements present must be taken into account. The formula of a compound is written by placing side by side the symbols of the constituent elements in proper order and putting a numerical subscript to the immediate right and below of each of the symbols to indicate the number of atoms of that particular element present. A subscript of 1 is never inserted in the formula.

A molecule of carbon dioxide contains one atom of carbon and two atoms of oxygen. So, the formula of carbon dioxide is CO_2 . The formula of cane sugar is $C_{12}H_{22}O_{11}$ as the molecule of it is made up of 12 atoms of carbon, 22 atoms of hydrogen and 11 atoms of oxygen.

A number placed to the left of a formula indicates the number of molecules of the substance. Thus $2H_2O$, $3H_2O$, $x H_2O$ express two, three and x molecules of water respectively.

N. B. It must be clearly understood that a formula stands for only one molecule of the substance but never indicates the substance itself. The formula H_2O represents a single molecule of water and cannot be used to express even for a drop of water. It has been calculated that a drop of water weighing 0.04 gm contains 1.338×10^{21} molecules of it.

2. It is to be noted that a conventional rule is followed in the order of placing the symbols of different elements in the formula of a compound. Generally, the symbols are arranged according to the decreasing electropositive character of the elements, i.e. the symbol of more electropositive element is written first. Of course exceptions to it are also observed.

Complete meaning of a formula : A chemical formula has qualitative as well as quantitative aspects.

Qualitatively, it denotes the name of the substance and indicates the elements of which the substance is constituted.

From the quantitative point of view, it represents—

(a) One molecule of the substance and the number of atoms of the element or elements present in one molecule of the substance.

(b) the molecular weight (or formula weight) of the substance.

(c) relative weights of the elements present in the molecular weight of the compound.

(d) one gm-molecule or one mole (when the weight is expressed in gm)

(e) In the case of a gaseous substance, the formula also denotes a volume equal to 22.4 litres at N.T.P (mol. wt. expressed in gm.)

Examples :

1. The formula, Cl_2 conveys the following information—

(a) It indicates chlorine.

(b) It stands for one chlorine molecule which is made up of two atoms of chlorine.

(c) It represents 35.5×2 or 71 parts by weight (molecular weight) of chlorine.

(d) It indicates unit volume and a volume equal to 22.4 litres at N.T.P. (wt. to be expressed in gm).

2. The formula, MgCO_3 supplies the following qualitative and quantitative information :

(a) It stands for the name of the compound magnesium carbonate. (b) It indicates that magnesium carbonate is made up of three elements viz. magnesium, carbon and oxygen. (c) It stands for one magnesium carbonate molecule consisting of one atom of magnesium, one atom of carbon and three atoms of oxygen i.e., the atomic ratio of the constituent elements is 1 : 1 : 3. (d) It represents $(1 \times 24 + 12 + 3 \times 16)$ or 84 parts by weight (molecular weight) of the compound. It further denotes one gm molecule or one mole (when molecular weight is expressed in gm) of magnesium carbonate. (e) It also tells us that 84 parts by weight of magnesium carbonate contain 24 parts by weight of magnesium, 12 parts by weight of carbon and 48 parts by weight of oxygen.

Valency : Compounds are formed by chemical combination of atoms of different elements in simple numerical proportions. It is however observed that the combining ability of atoms of different

elements is not the same. Analysis of a number of hydrogen-compounds reveals that atoms of different elements combine with one or more atoms of hydrogen. Thus,

Compound	Formula	Number of H atoms taking part in combination
Hydrogen chloride	HCl	1 (1 atom of chlorine combines with 1 atom of hydrogen)
Water	H ₂ O	2 (1 atom of oxygen combines with 2 atoms of hydrogen)
Ammonia	NH ₃	3 (1 atom of nitrogen combines with 3 atoms of hydrogen)
Methane	CH ₄	4 (1 atom of carbon combines with 4 atoms of hydrogen)

Similar is the case when we examine the compounds of different elements with chlorine.

Chlorine-compound	Formula	Number of Chlorine atoms combining with 1 atom of another element
Hydrogen chloride	HCl	1
Magnesium chloride	MgCl ₂	2
Aluminium chloride	AlCl ₃	3
Platinic chloride	PtCl ₄	4
Phosphorus pentachloride	PCl ₅	5

From the above hydrogen-compounds, it is clear that atoms of different elements have different capacities for combining with hydrogen. Based on this fact, the chemists have measured the combining power or valency which atoms of different elements possess. Results of analysis of hydrogen-compounds further confirm that an atom of hydrogen has the least combining capacity as no hydrogen compound is available (except hydrazoic acid, N₃H) which contains one atom of hydrogen combined with more than one atom of any other element. So, for measuring the valencies of other elements hydrogen atom has been chosen as the standard and its combining capacity or valency is taken to be 1. Therefore, *the valency of an element may be regarded as its capacity for combining with other elements and is measured by the number of hydrogen atoms with which one atom of the given element can combine.*

Thus from the compounds, hydrogen chloride (HCl), water (H₂O), ammonia (NH₃), methane (CH₄), we can say that the valencies of chlorine, oxygen, nitrogen and carbon are 1, 2, 3 and

4 respectively. Similarly from hydrogen fluoride (HF), hydrogen bromide (HBr) and hydrogen iodide (HI), it is clear that the valency of each of the elements fluorine, bromine and iodine is 1.

There are elements that do not combine directly with hydrogen but displace it easily from a hydrogen-compound. Valency of such an element is equal to the number of hydrogen atoms displaced by one atom of the element. One atom of zinc displaces 2 atoms (1 molecule) of hydrogen from dilute sulphuric acid. Therefore, valency of zinc is 2.

✓ So, the valency of an element may be defined as the capacity of its atom to combine with atoms of other elements and is measured by the number of hydrogen atoms which can combine with or are displaced by one atom of the element in question.

When an element is incapable of combining with hydrogen directly, its valency may be determined with reference to chlorine or oxygen (the valencies of chlorine and oxygen are already known as 1 and 2 respectively).

The metals like sodium and potassium have greater affinity for chlorine than for hydrogen. It has been found that one atom of sodium or potassium combines with one atom of chlorine to form sodium chloride (NaCl) or potassium chloride (KCl). As the valency of chlorine is 1, the valency of either sodium or potassium will also be 1. From the compounds of chlorine stated in the previous table, we can say that the valencies of magnesium, aluminium and platinum are 2, 3 and 4 respectively. Gold is an element that does not directly combine with hydrogen or does not displace hydrogen from a hydrogen-compound. But it forms a chloride (AuCl_3) in which one atom of gold combines with three atoms of chlorine. Obviously, the valency of gold is 3. Sometimes, oxygen is used as a standard for determining valency. On the oxygen scale, the valency of an element becomes equal to twice the number of oxygen atoms combining with one atom of the element. Thus, the valency of carbon in carbon dioxide (CO_2) or sulphur in sulphur dioxide (SO_2) is 4. Similarly valency of magnesium in magnesium oxide (MgO) is 2.

N. B. (1) In the light of above discussions, it is better to modify the definition of valency as—

The valency of an element is a measure of its combining capacity and is equal to the number of atoms of hydrogen or chlorine or twice the number of atoms of oxygen combining with or displaced by one atom of the element.

(2) Valency is always expressed by integral numbers. It can never be a fraction.

Classification of elements according to their valencies: The element having valency equal to 1 is said to be a mono or uni-valent element. The element, an atom of which can combine with two atoms of hydrogen or two atoms of other univalent elements is referred to as the bivalent or divalent element. Similarly, the elements are classified as trivalent, tetravalent, pentavalent etc. according to

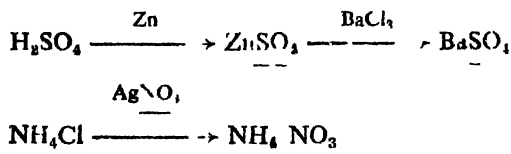
their valencies. The inert gases like helium, argon, neon etc. ordinarily form no compound with other elements and their valency or combining capacity is taken to be zero. These elements are designated as zerovalent elements.

In the following table, classification of some of the common elements according to their valencies has been shown.

Valency		Elements
0	Zerovalent	Helium, Argon, Neon, Krypton etc.
1	monovalent	Hydrogen, Fluorine, chlorine, Bromine, Iodine, Sodium, Potassium, Silver, Copper (cuprous) Mercury (mercurous) etc.
2	bivalent	Oxygen, Sulphur, Calcium, Magnesium, Zinc, Barium, Copper (cupric), Tin (stannous), Mercury (mercuric), Manganese (manganous), Iron (ferrous), Lead (plumbous) etc.
3	trivalent	Nitrogen, phosphorus, Boron, Aluminium, Arsenic, Gold, Iron (ferric), Chromium, (chromic) etc.
4	tetravalent	Carbon, Silicon, Sulphur, Tin (Stannic), Platinum, Lead (plumbic), Manganese etc.
5	pentavalent	Nitrogen, Arsenic, Phosphorus etc.
6	hexavalent	Sulphur, Chromium, Manganese etc.
7	heptavalent	Chlorine, Manganese etc.
8	Octavalent	Osmium.

Compound radicals and their valencies :

It is found that some groups of atoms of different elements occur intact in the molecules of a number of compounds. They behave collectively like single atoms, take part as a whole in chemical reactions but have necessarily no separate existence. Such a group of elements is known as a compound radical or simply a radical. Thus,



From the above examples, it is clear that SO_4 (sulphate), NH_4 (ammonium) and NO_3 (nitrate) are three distinct radicals.

The idea of valency has been extended to the cases of radicals.

Names of some familiar radicals and their classification in respect of valency are given below.

Valency	Radicals.
1. monovalent	OH (hydroxyl), NH_4 (ammonium), NO_3 (nitrate), NO_2 (nitrite), HCO_3 (bicarbonate), HSO_4 (bisulphate), HSO_3 (bisulphite), CN (cyanide), MnO_4 (permanganate), ClO_3 (chlorate) etc.
2. bivalent	SO_4 (sulphate), SO_3 (sulphite) CO_3 (carbonate), CrO_4 (chromate), Cr_2O_7 (dichromate) etc
3. trivalent	PO_4 (phosphate), AsO_4 (arsenate), $\text{Fe}(\text{CN})_3$ [ferricyanide] etc.
4. tetravalent	$\text{Fe}(\text{CN})_6$ [ferrocyanide] etc.

Variable Valency: The valency of an element is not always constant. There are some non-metallic and metallic elements which have more than one valency. Different valencies shown by nitrogen, phosphorus, sulphur, copper, iron, mercury etc. are tabulated below.

Element	Valency	Element	Valency
Nitrogen	3, 5	Copper	1, 2
Phosphorus	3, 5	Mercury	1, 2
Sulphur	2, 4, 6	Tin	2, 4
Chlorine	1, 7	Iron	2, 3

An inspection of the formulae of the stable oxides and chlorides given in the following table leads to the conclusion that phosphorus and iron may display variable valency.

Element	Valency	Formulae of oxides	Formulae of chlorides
Phosphorus	3	P_2O_3 (Phosphorus trioxide)	PCl_3 (Phosphorus trichloride)
	5	P_2O_5 (Phosphorus pentoxide)	PCl_5 (Phosphorus pentachloride)
Iron	2	FeO (Ferrous oxide)	FeCl_2 (Ferrous chloride)
	3	Fe_2O_3 (Ferric oxide)	FeCl_3 (Ferric chloride)

It is evident that phosphorus (or iron) may exhibit variable valency in its compounds with the same element. Elements like nitrogen, phosphorus, sulphur etc may show variation in valency in their compounds with hydrogen and oxygen. Thus, sulphur is divalent in hydrogen sulphide (H_2S), tetravalent in sulphur dioxide (SO_2) and hexavalent in sulphur trioxide (SO_3). Similar variation will be observed when the hydrides and oxides of nitrogen or phosphorus are examined.

An element that possesses different valencies and is capable of uniting with both hydrogen and oxygen will exert its minimum valency in the hydrogen-compound and the maximum in the compound with oxygen. Moreover, the sum of the two valencies (minimum and maximum) is generally found to be 8. This is known as *Abegg and Bodlander rule*.

Compounds	Sum of valencies
HCl (Valency of chlorine in hydrogen compound is 1)	1+7=8
Cl ₂ O ₇ (" " " " oxygen " " 7)	
H ₂ S (" " sulphur " hydrogen " " 2)	2+6=8
SO ₃ (" " " " oxygen " " 6)	
NH ₃ (" " nitrogen " hydrogen " " 3)	3+5=8
N ₂ O ₅ (" " " " oxygen " " 5)	
PH ₃ (" " phosphorus " hydrogen " " 3)	3+5=8
P ₂ O ₅ (" " " " oxygen " " 5)	

Practical application of valency : The classification of elements and radicals according to their valencies is of great importance in the study of chemistry. The knowledge of valency is mainly used in writing correct formulae of the compounds. It is seen that (i) one atom of a univalent element or a univalent radical combines with one atom of another univalent element or with other univalent radical, e.g., NaCl, HCl, NH₄Cl, NH₄NO₃, KOH, HNO₃ etc. (ii) One atom of a bivalent element or a bivalent radical combines with two atoms of a univalent element or two univalent radicals ; one atom of a divalent element is found to unite with one atom of another divalent element or with another divalent radical, e.g., H₂O, CaCl₂, H₂SO₄, MgO, CaS, ZnSO₄ etc. (iii) One atom of a trivalent element or a trivalent radical unites with three atoms of a univalent element or three univalent radicals : one atom of a trivalent element combines with one atom of another trivalent element or a trivalent radical, e.g. NH₃, AlCl₃, Al(OH)₃, H₃PO₄, AlN, and AlPO₄.

Two atoms of a trivalent element combine with three atoms of a bivalent element, e.g., Al₂O₃, Fe₂O₃, etc.

The same rule can be applied in the cases of tetra, penta and hexavalent elements. On inspection of the above facts, we can arrive at a general rule of writing the formula of a compound consisting of two elements, two radicals or one element and one radical.

If two elements A and B combine with each other to form a compound and if x be the valency of A and y be the valency of B, the formula of the resulting compound will be A _{$\frac{y}{x}$} B _{$\frac{x}{y}$} . Thus, in the formula of the compound, the valencies of the elements are interchanged and the numerical subscript denoting the valency of A is written to immediate right and a little below of B. The subscript denoting the valency of B is similarly placed by the right of A.

This has been illustrated in the Fig. 1(17) by placing the respective valencies on the top of A and B.

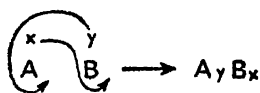


Fig. 1(17)

This is to be noted further that in the compound of A and B, the valencies of both A and B are mutually satisfied so that the valency of the compound as a whole is zero ; hence the total valency of A must be equal and opposite to that of B.

Thus, Total valency of A = Total valency of B

or, Number of atoms of A \times valency of A = Number of atoms of B \times valency of B,

or,
$$\frac{\text{Valency of A}}{\text{Valency of B}} = \frac{\text{Number of atoms of B}}{\text{Number of atoms of A}}$$

Therefore the formula of a binary compound (a compound of two elements) will contain atoms of the constituent elements in the inverse ratio of their valencies.

The same rule also holds good when combination takes place between two radicals or one element and one radical.

When the valencies of the two elements (or radicals) are found divisible by a common factor, they are first reduced to a simple ratio and then the above procedure is applied to get the formula. A subscript of 1 (indicating valency) need not be written in the formulae.

The definition of valency, however, fails to represent certain facts. Carbon and hydrogen combine together to form a series of compounds such as C_2H_2 , C_2H_4 , C_2H_6 , CH_4 in which the apparent valency of carbon is 1, 2, 3 and 4 respectively. But carbon is always tetravalent in all of its compounds.

Critical observation of the following compounds will help us in writing correct formulae of the compounds and to be familiar with the valencies of the most common elements and radicals. The valencies of the constituent elements (or radicals) have been shown in brackets by the side of the symbols representing the elements or radicals

Name of compound	Formula
Sodium hydride, Na(1)H(1)	— $Na_1H_1 = NaH$
Ferric oxide, Fe(3)O(2)	— Fe_2O_3
Magnesium nitride, Mg(2)N(3)	— Mg_3N_2
Phosphorus pentoxide, P(5)O(2)	— P_2O_5
Aluminium chloride, Al(3)Cl(1)	— $Al_1Cl_3 = AlCl_3$
Ammonium chloride, NH ₄ (1)Cl(1)	— NH_4Cl
Stannous chloride, Sn(2)Cl(1)	— $SnCl_2$
Stannic chloride, Sn(4)Cl(1)	— $SnCl_4$
Sodium hydroxide, Na(1)OH(1)	— $NaOH$
Ammonium nitrate, NH ₄ (1)NO ₃ (1)	— NH_4NO_3
Silver nitrite, Ag(1)NO ₂ (1)	— $AgNO_2$

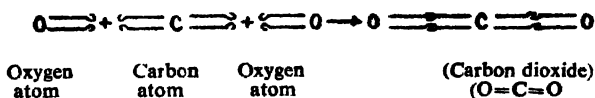
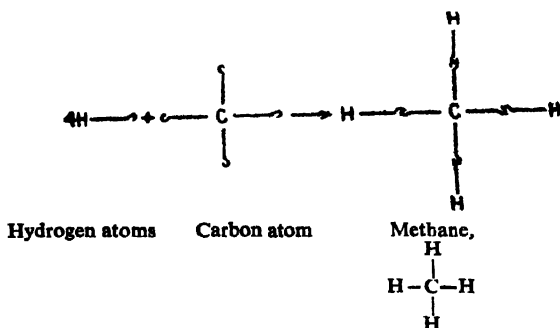
Name of compound		Formula
Sodium phosphate, Na(1)PO ₄ (3)	—	Na ₃ PO ₄
Calcium phosphate, Ca(2)PO ₄ (3)	—	Ca ₃ (PO ₄) ₂
Aluminium phosphate, Al(3)PO ₄ (3)	—	Al ₃ (PO ₄) ₃ = AlPO ₄
Zinc sulphate, Zn(2)SO ₄ (2)	—	Zn(SO ₄) ₂ = ZnSO ₄
Aluminium sulphate, Al(3)SO ₄ (2)	—	Al ₂ (SO ₄) ₃
Sodium bisulphate, Na(1)HSO ₄ (1)	—	NaHSO ₄
Potassium carbonate, K(1)CO ₃ (2)	—	K ₂ CO ₃
Potassium bicarbonate, K(1)HCO ₃ (1)	—	KHCO ₃
Sodium sulphite, Na(1)SO ₃ (2)	—	Na ₂ SO ₃
Calcium bisulphate, Ca(2)HSO ₄ (1)	—	Ca(HSO ₄) ₂
Potassium permanganate, K(1)MnO ₄ (1)	—	KMnO ₄
Potassium dichromate, K(1)Cr ₂ O ₇ (2)	—	K ₂ Cr ₂ O ₇
Potassium chromate, K(1)CrO ₄ (2)	—	K ₂ CrO ₄
Potassium chlorate, K(1)ClO ₃ (1)	—	KClO ₃
Silver perchlorate, Ag(1)ClO ₄ (1)	—	AgClO ₄
Potassium ferrocyanide, K(1)[Fe(CN) ₆](4)	—	K ₄ Fe(CN) ₆
Potassium ferricyanide, K(1)[Fe(CN) ₆](3)	—	K ₃ Fe(CN) ₆

N. B : Generally, the valencies of electropositive metals (including hydrogen and ammonium radical) are referred to as positive valencies and those for non-metals and other radicals are called negative valencies

Structural formula or Graphic formula :

In order to indicate easily the linking or arrangement of the different atoms in a molecule, the valency of an atom is represented by a necessary number of hyphens or small straight lines drawn from its symbol. A symbol of a monovalent element will have one hyphen. A symbol with two hyphens will represent the atom of a bivalent element and so on. Thus—

Atom	Valency	Graphical representation
H	1	H—
O	2	—O—
Mg	2	—Mg—
N	3	—N—
P	3	—P—
C	4	—C—

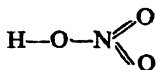


Thus, the formula showing a complete picture as to how the various atoms are linked to each other in the molecule with the aid of their valencies is known as structural formula. A few illustrations are given below.

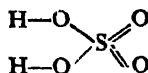
molecular formula

structural formula

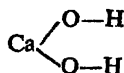
HNO_3
nitric acid



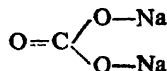
H_2SO_4
sulphuric acid



$\text{Ca}(\text{OH})_2$
calcium hydroxide



Na_2CO_3
sodium carbonate



N. B. (1) It must be remembered that the hyphens, hooks or bonds in the form of dashes do not really exist. They are only used to indicate the internal arrangement of atoms in a molecule.

(2) This type of graphic representation is not always correct from the standpoint of modern conception of valency.

Nomenclature of compounds :

In naming a binary compound, i.e. a compound formed by the union of two elements only, the more electropositive element is

named first and the other element is named after that with a suffix *ide*. In the case of a compound consisting of two non-metals, it is customary to begin its name with the name of the solid non-metal.

The compounds of oxygen with other elements are known as oxides. Similarly, the binary compounds of sulphur, hydrogen, nitrogen, chlorine, bromine and iodine with other elements are called sulphides, hydrides, nitrides, chlorides, bromides and iodides respectively. Phosphorus in combination with a metal gives the compound named as a phosphide and the carbides are binary compounds of carbon with metals.

Some examples are given below :

Zinc oxide— ZnO	Magnesium nitride— Mg_3N_2
Sodium sulphide— Na_2S	Aluminium chloride— AlCl_3
Hydrogen sulphide— H_2S	Calcium bromide— CaBr_2
Calcium carbide— CaC_2	Potassium iodide— KI
Sodium hydride— NaH	Calcium phosphide— Ca_3P_2

If an element exhibits variable valency, the different compounds formed by it are distinguished by using the suffixes 'ous' and 'ic' at the end of its name. The suffix 'ous' stands for lower valency while 'ic' for the higher valency.

Cuprous oxide— Cu_2O (Valency of copper is 1)	Cupric oxide— CuO (Valency of copper is 2)
Ferrous chloride— FeCl_2 (Valency of iron is 2)	Ferric chloride— FeCl_3 (Valency of iron is 3)
Nitrous oxide— N_2O [Valency of nitrogen is 1]	Nitric oxide— NO [Valency of nitrogen is 2]

Sometimes, prefixes mono, di, tri etc. are used before the name of the more electronegative element to indicate its number of atoms present in the molecule.

Carbon monoxide— CO	Carbon dioxide— CO_2
Lead monoxide— PbO	Lead dioxide— PbO_2
Phosphorus trichloride— PCl_3	Phosphorus pentachloride— PCl_5

In naming a metallic compound containing a radical, the metallic element (including ammonium radical) is named first, such as sodium hydroxide NaOH , ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$. The formula containing one or more hydrogen atoms before a radical represents an acid. Thus, sulphuric acid is H_2SO_4 ; phosphoric acid, H_3PO_4 ; carbonic acid, H_2CO_3 ; nitric acid, HNO_3 .

Chemical Equations : A chemical reaction is the change suffered by one or more substances in composition to produce one or more new substances with new properties. We have already seen that the elements and compounds are expressed briefly by their symbols and formulae respectively. Similarly, the chemists have devised a shorthand system which is intended to represent a chemical reaction

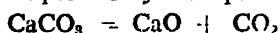
symbolically. This system uses symbols and formulae of the substances instead of words. Such symbolic expression standing for a chemical reaction is termed a chemical equation. As each of the symbols and formulae used will stand for certain weight, an equation will reveal both qualitative and quantitative aspects of a reaction. Thus—

The short hand method of representation of a true chemical reaction expressing its qualitative as well as quantitative aspects with the help of symbols and formulae is called a chemical equation.

In a chemical equation, the formulae (and symbols) of the reacting substances (reactants) connected by plus (+) signs are to be written on the left and the formulae (and symbols) of the products with plus (+) signs in between them are to be put on the right. The set of reactants is separated from that of the products by a sign of equality (=). The plus (+) sign on the left hand side of the sign of equality indicates "*reacts with*" and that on the right means "*and*". The sign of equality is interpreted as "*to produce*". Thus the equation



is the symbolic representation of the statement that zinc reacts with sulphuric acid to produce zinc sulphate and hydrogen. That calcium carbonate changes chemically to produce calcium oxide and carbon dioxide is expressed by the equation,



Quantitative aspects of an equation have been discussed later.

How are chemical equations written correctly :

In writing a correct equation, the following points are to be borne in mind.

(1) A chemical equation is meant for expressing the experimental facts and must represent a chemical change that actually takes place. In other words chemical equation must represent a *true* chemical reaction. If a reaction is not possible between certain substances, it cannot be represented by a chemical equation.

(2) In framing the equation, one must know what substances are reacting i.e. (reactants) and what are the products formed as a result of the reaction.

(3) All substances (both elementary and compound) appearing in an equation are to be put in the form of their molecular formulae.

Obviously, elementary gases like hydrogen, oxygen, nitrogen, chlorine etc are to be written as H_2 , O_2 , Cl_2 and N_2 respectively. But the monatomic molecules of sodium and mercury are represented by their symbols, i.e. by Na and Hg. For solid metals and non-metals, of unknown atomicity, symbols are used. Thus, alumin-

um, magnesium, iron, tin, boron, silicon, carbon are represented by Al, Mg, Fe, Sn, B, Si, C respectively in the equation. So, it is not possible to write a correct equation unless the correct formulae and symbols of the reactants and the products are known.

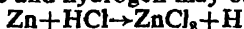
(4) The formulae (and symbols) of reactants and the products are to be placed properly as already described.

(5) To conform to the law of conservation of mass, an equation must be balanced (if necessary) by putting smallest, simple integral balancing numbers called coefficients before the formulae (and symbols). It is done in such a way that the same number of atoms of each element appears on both sides of the sign of equality. The coefficients represent the number of molecules that react and are produced. Thus, the equalization of atoms of each element taking part in the reaction either as such or in the form of any of its compounds on both sides of the equation is known as the *balancing of an equation*.

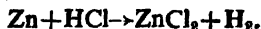
The equation which contains an equal number of atoms of each element on either side is called a *balanced equation*.

Balancing of equations is done either by (1) method of inspection or (2) method of partial equations. How to arrive at a balanced chemical equation of a reaction by the applying the method of inspection or trial is shown below.

The action of dilute hydrochloric acid on commercial zinc to produce zinc chloride and hydrogen may be symbolically represented as



Such an equation which simply represents the reactants and the products of the reaction by the symbols and the formulae of the elements and compounds taking part therein irrespective of the unequal number of atoms of any element on either side is called a *skeleton equation*. This is not the correct form of the equation as hydrogen, an elementary gas, appears in it in the atomic form. So, hydrogen must be brought to its normal molecular form as H_2 . In doing so, the equation assumes the form :



The above molecular equation which is the main skeleton equation is still incorrect as the number of hydrogen atoms and that of chlorine atoms are not equal on both sides. Obviously, this form of equation is not in agreement with the law of conservation of mass. Now, by inspection, we see that if two molecules of HCl are taken, the above equation assumes the final balanced form :



So, to get the balanced equation of a reaction, the main skeleton equation in which the smallest stable particles i.e. atoms and molecules of the reactions and the products are represented by

their symbols and formulae is to be framed first. Finally, the symbols and the formulae used in the skeleton equation are to be multiplied by suitable smallest numbers so that the number of atoms of each element appearing on both sides of the equation becomes the same. A regular practice of the method of trial or inspection enables one to balance most of the chemical equations.

A few more illustrations of equations *balanced by method of inspection* are given below

(A) Hydrogen and oxygen combine chemically to produce water i.e.

Hydrogen + Oxygen = water.

$\text{H} + \text{O} \rightarrow \text{H}_2\text{O}$ (using symbols of atoms of the elements and formula of the compound – skeleton equation)

$\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$ (expressing each by formula – unbalanced molecular equation)

$2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ (using coefficients to make the number of atoms equal on both sides of the sign of equality. This is the required correct balanced equation)

(B) Iron at red heat reacts with steam to produce ferrous-ferrous oxide and hydrogen.

$\text{Fe} + \text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_4 + \text{H}$

$\text{Fe} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$

$3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$ (correct equation)

(C) Potassium chlorate breaks up producing potassium chloride and oxygen on heating.

$\text{KClO}_3 \rightarrow \text{KCl} + \text{O}$

$\text{KClO}_3 \rightarrow \text{KCl} + \text{O}_2$

Here, 3 atoms of oxygen are on the left and 2 oxygen atoms are on the right.

Multiplying the formula of the reactant by 2, we get

$2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$ (correct balanced equation.)

(D) Silver nitrate reacts with calcium chloride to produce silver chloride and calcium nitrate.

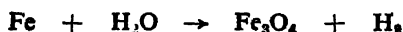
$\text{AgNO}_3 + \text{CaCl}_2 \rightarrow \text{AgCl} + \text{Ca}(\text{NO}_3)_2$

It is clear that 2 molecules of silver nitrate are necessary to supply 2 silver atoms for combining with 2 atoms of chlorine present in a CaCl_2 -molecule. Hence, the required balanced equation will be

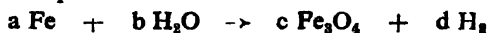
$2\text{AgNO}_3 + \text{CaCl}_2 = 2\text{AgCl} + \text{Ca}(\text{NO}_3)_2$

The co-efficients to be used before the formulae (and symbols) in a balanced equation can be determined easily by algebraic method.

To explain the method, let us consider again the reaction between the red hot iron and steam. The unbalanced molecular equation of the reaction is

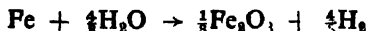


If a, b, c, d are written as the co-efficients before the symbol and formulae, the equation becomes

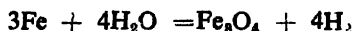


The number of Fe atom on the left hand side of the arrow is 1 and the number of Fe atoms on the right hand side 3. As the number of atoms of any element must be equal on both sides of the equation, a must be equal to $3c$. For similar reason, in the case of hydrogen atoms, $2b = 2d$ or $b = d$ and in the case of oxygen-atoms $b = 4c = \frac{4}{3}a$. Now if the value of any co-efficient say a is taken to be 1, $c = \frac{1}{3}$, $b = \frac{4}{3}$ and $d = \frac{4}{3}$.

By putting the values of a, b, c and d , the equation assumes the following form



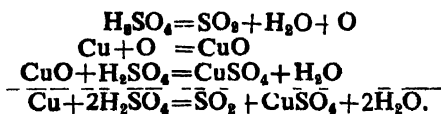
So, multiplying both sides by 3, we get the following balanced equation.



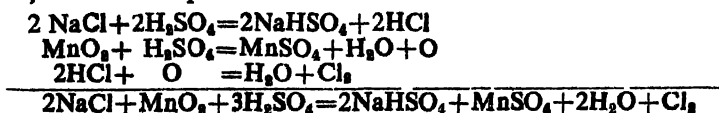
By simple inspection, it is often a difficult task to balance the equations representing the complicated types of reactions. In such a case, the equation is divided into a number of imaginary but possible intermediate stages each of which is represented by a separate equation (balanced by inspection) called partial equation. The balanced equation is finally arrived at by adding the partial equations in such a way that the intermediate products are cancelled and do not appear in the final equation. For correct balancing of the final equation, the partial equations are sometimes, required to be multiplied by proper integers.

The *partial equation method* of balancing equation is illustrated by a few examples.

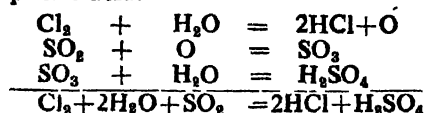
(A) Copper turnings react with hot concentrated sulphuric acid producing sulphur dioxide. The other products are copper sulphate and water.



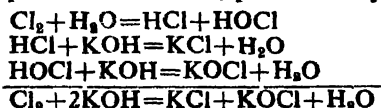
(B) When heated, manganese dioxide, sodium chloride and conc. sulphuric acid react together to form manganous sulphate, chlorine, sodium bisulphate and water.



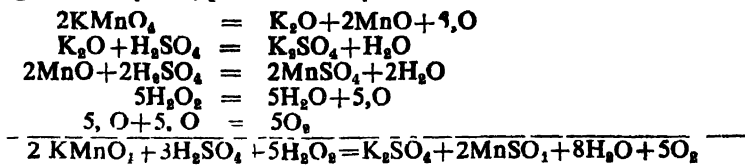
(C) Chlorine converts an aqueous solution of sulphur dioxide into sulphuric acid.



(D) Chlorine reacts with a cold solution of potassium hydroxide to give potassium chloride, potassium hypochlorite and water.



(E) Potassium permanganate reacts with hydrogen peroxide in acid solution producing gaseous oxygen. Other products are manganous sulphate, potassium sulphate and water.



To understand this method, a student must have a sound knowledge about oxidation-reduction and acid-base neutralisation.

Significance of a chemical equation :

Every chemical equation has a qualitative and quantitative significance.

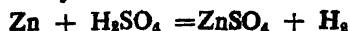
Qualitatively, it signifies what substances are reacting there in and are produced in a chemical reaction.

Quantitatively, it tells us

[a] the relative number of atoms and molecules taking part and produced in a chemical reaction.

[b] ratio of the weights, number of moles and volumes [in the case of gases] in which the substances interact and the relative weights, moles and volumes [for gaseous substances] of the products formed. Practically a balanced chemical equation represents a quantitative relation between the reactants and the resultants [products] and the two fundamental laws of chemistry (the law of definite proportions and the law of conservation of mass) and the Dalton's atomic theory are chiefly expressed in it. Significance of a chemical equation will be well understood from the following examples.

(A) *Equation of the reaction between zinc and sulphuric acid :*



The above equation indicates : [i] Zinc and sulphuric acid react chemically to produce zinc sulphate and hydrogen.

[ii] One atom* of zinc reacts with one molecule of sulphuric acid to form one molecule of zinc sulphate and one molecule of hydrogen.

[iii] The total number of atoms present in the reactants [viz. $1+2+1+4=8$] on the left side is equal to the total number of atoms present in the products [viz. $1+1+4+2=8$] on the right side of the equation.

[iv] 65.4 parts by weight of zinc [at. wt. of Zinc is 65.4] react with 98 parts by weight of sulphuric acid (mol. wt. of $\text{H}_2\text{SO}_4=98$) to produce 161.4 parts by weight of zinc sulphate and 2 parts by weight of hydrogen.

(v) 65.4 gms of zinc (one gm.-atom) react with 98 gms of sulphuric acid (one gm.-molecule) to form 161.4 gms. (one gm.-molecule) of zinc sulphate and 2 gms. (one gm-molecule) of hydrogen.

(vi) 65.4 gms of zinc (1 mole) reacts with 98 gms of sulphuric acid (1 mole) to form 161.4 gms (1 mole) of zinc sulphate and 22.4 litres of hydrogen at N.T.P.

(vii) The total weight of the reactants (viz. $65.4+2 \times 1+32+4 \times 16$) before the reaction is equal to the total weight of the resultants (viz. $65.4+32+4 \times 16+2 \times 1$) after the reaction.

(B) An equation involving gaseous substances :



The above equation gives us the following information.

(i) Nitrogen and hydrogen combine chemically to produce ammonia. (ii) One molecule of nitrogen combines with three molecules of hydrogen to form two molecules of ammonia. (iii) The total number of atoms present in the reactants (viz. $2+3 \times 2=8$) on the left hand side is equal to the total number of atoms present in the products [viz. $2(1+3)=8$] on the right hand side of the equation. (iv) 2×14 or 28 parts by weight of nitrogen combine with 3×2 or 6 parts by weight of hydrogen to produce 2×17 or 34 parts by weight of ammonia (v) 2×14 gms. (1 gm-molecule) of nitrogen combine with 3×2 gms (3 gm-molecules) of hydrogen to form 2×17 gms (2 gm-molecules) of ammonia. (vi) Under the same condition of temperature and pressure, one volume of nitrogen combines with three volumes of hydrogen to produce two volumes of ammonia. (vii) At N. T. P., 22.4 litres of nitrogen and 3×22.4 litres of hydrogen react to produce 2×22.4 litres of ammonia. (viii) The total

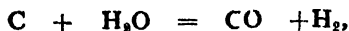
* Zinc being a solid element, the molecule of it is denoted by its symbol.

weight of the reactants [viz. $2 \times 14 + 3 \times 2$] before the change is equal to the total weight of the products [viz. $2[14 + 3 \times 1]$ after the change.

Limitations of a chemical equation :

Although a chemical equation summarises many facts and supplies many valuable information regarding a chemical reaction, it has got certain limitations. For example—

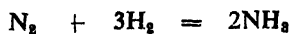
(i) A chemical reaction cannot tell us the physical state (solid, liquid or gaseous) of the reactants and the products. Thus, in the equation,



there is no indication regarding the physical states of the substances involved in the reaction.

(ii) It cannot provide any information about the energy change taking place during a chemical reaction. In other words, it is not possible to know from an equation whether a reaction is exothermic or endothermic.

The combination of hydrogen and nitrogen takes place with evolution of 24,000 cal. of heat. But the equation depicting the combination,

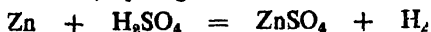


does not indicate the thermal change.

(iii) The conditions (whether the reaction requires application of heat, pressure, electricity etc. or presence of a catalyst) necessary for the reaction are not known from the equation. Best yield of ammonia is obtained if the reaction represented by the equation $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ is carried out at a temperature of 550°C , under a pressure of 200 atmos. and in presence of iron powder used as a catalyst. But the equation does not provide any such information.

(iv) The equation does not tell the rate or speed at which the reaction proceeds and the time required for its completion.

(v) The concentrations of the reacting substances are not expressed in an equation. We know that when zinc is added to dilute sulphuric acid, hydrogen is evolved. But the equation,



does not give any idea regarding the concentration of the acid.

(vi) The equation fails to tell us whether a reaction is reversible i.e. whether the products recombine to give the original reactant or reactants. Ammonium chloride when heated produces ammonia and hydrogen chloride which reunite on cooling to give ammonium chloride. This fact is not expressed in the equation,

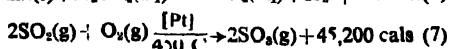
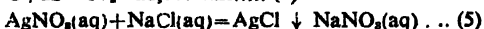
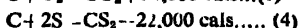
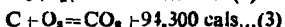
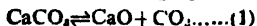


(vii) The equation does not indicate the change of colour of the substances involved in the reaction and its mechanism.

N. B. The students should be familiar with some specific notations, now a days used in equations to express the nature of the reactions, energy changes and the physical conditions of the substances involved in reactions.

For a reversible reaction the sign '=' in the equation is replaced by the sign ' \rightleftharpoons '. The pair of oppositely directed arrows is known as the sign of reversibility. The sign \downarrow placed to the right side of a product indicates its precipitation. Similarly, the sign \uparrow denotes the evolution of the substance in gaseous form. The symbols such as s, l, g are used respectively to indicate the solid, liquid and gaseous states of the reactants and the products. The symbol 'aq' (aqua = water) implies that the substance indicated is in aqueous solution.

Let us consider the following equations :



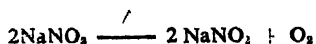
Decomposition of calcium carbonate into calcium oxide and carbon dioxide and combination of hydrogen and iodine to give hydrogen iodide are reversible processes [as shown in eqns (1) and (2) respectively].

The equation (3) states that when 1 mole of carbon reacts with 1 mole of oxygen till completion, 1 mole of carbon dioxide is produced and 94,300 calories of heat are evolved. It is an exothermic reaction. Similarly, equation (4) expresses that the combination of 1 mole of carbon and 2 moles of sulphur yields 1 mole of carbon disulphide with absorption of 22,000 cal of heat. It is an endothermic reaction.

The equation (5) above shows that aqueous solutions of silver nitrate and sodium chloride react to produce silver chloride which is precipitated and sodium nitrate which remains in solution. The equation (6) tells us that solid zinc reacts with aqueous solution of sulphuric acid to evolve gaseous hydrogen and to form zinc sulphate which remains in solution :

The equation (7) states that (i) sulphur dioxide and oxygen both in gaseous state react together to produce sulphur trioxide gas. (ii) the reaction occurs in presence of platinum that acts as a catalyst. (iii) it takes place at a temperature of 450°C and (iv) it is an exothermic reaction evolving 45200 cal of heat during formation of every 2 moles of sulphur trioxide.

The Greek symbol Δ is now commonly used to indicate that a particular reaction proceeds with the agency of heat.

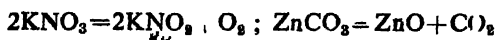


Brief discussion on the important types of chemical reactions :

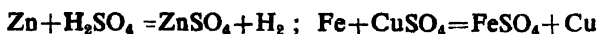
(1) *Synthesis or Combination* : The process in which a compound is formed by the direct union of its constituents is termed synthesis or combination. When carbon is heated in oxygen, direct union between the two elements takes place to produce carbon dioxide. Metallic magnesium at red heat directly unites with nitrogen to form magnesium nitride.



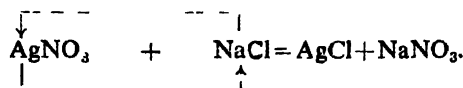
(2) **Decomposition or Analysis :** The process is termed decomposition when a compound is converted into two or more simpler substances with altogether new properties. Potassium nitrate on heating decomposes into potassium nitrite and oxygen. Zinc carbonate when heated produces zinc oxide and carbon dioxide. It is the reverse of combination



(3) **Substitution or Displacement** : The substitution is a process in which one element from a compound is expelled by a more active element which subsequently takes the place of the element expelled. When zinc is added to sulphuric acid (dilute), it displaces hydrogen from the acid and takes its place forming zinc sulphate. A clean piece of iron dipped in copper sulphate solution displaces copper as red deposit and goes into the solution to form ferrous sulphate.



(4) **Double decomposition or Metathesis** : The process where two compounds react to produce two new compounds by mutual exchange of their constituent parts is called double decomposition. When a solution of silver nitrate is added to a solution of sodium chloride, we get the precipitate of silver chloride and sodium nitrate in solution.



Similarly, $\text{BaCl}_2 + \text{H}_2\text{SO}_4 = \text{BaSO}_4 + 2\text{HCl}$.



(5) Addition reaction : It is a reaction in which the molecule of a compound adds directly to the molecule of a different substance and no part of any of the reacting molecules is separated. The product thus formed is known as an addition product.

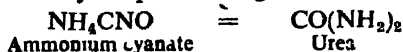


Carbon monoxide

Chlorine

Carbonyl chloride

(6) **Molecular rearrangement—Isomerisation:** It is a process in which due to change of conditions, the atoms present in the molecule of a compound may internally rearrange themselves to produce new compound having the same percentage composition but different properties. Thus, ammonium cyanate when heated, changes into urea by simple rearrangement of atoms.

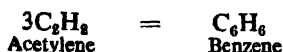


Ammonium cyanate

Urea

(7) **Polymerisation** : The union of two or more molecules of a simple substance to produce the complex molecule of another substance is known as polymerisation and the product thus formed.

is called a polymer of the simple substance. When acetylene is passed through a red hot tube, three molecules of it combine with each other to form a molecule of benzene.

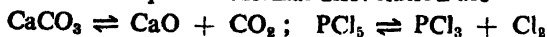


- ✓ (8) *Dissociation*: There are two main types of dissociation—
(a) Thermal dissociation and (b) Electrolytic dissociation.

The thermal dissociation is a process in which a substance breaks up into simpler different substances on heating but the products thus formed recombine to form the original substance on cooling. When ammonium chloride is heated, a molecule of it splits up into a molecule of ammonia and a molecule of hydrogen chloride but on cooling, the dissociated products i.e. ammonia and hydrogen chloride reunite to give ammonium chloride. This type of reaction is referred to as a *reversible reaction* and is represented as



Similar examples of thermal dissociation are—



The process of electrolytic dissociation and other types of reactions such as neutralisation, hydrolysis, oxidation-reduction reaction, catalytic reaction etc. will be discussed in different chapters of this book.

Chemical calculations

Calculation from chemical equations involving weights of reactants and products:

The quantitative aspects of a chemical equation have already been discussed. Since each of the symbols and formulae involved in a chemical equation represents a definite weight (usually in grams), the ratio of the weights in which substances interact and the relative weights of the products formed can be computed from it.

Thus, from a correctly balanced equation, we can easily find out either the weights of the products formed from the given weights of the reactants used or the weights of the reactants required to produce the given weights of the products.

In solving the problems based on weight relationship of the reactants and the products, the following method is to be adopted.

1. Correct equation representing the chemical reaction is to be written.
2. Atomic and molecular weights of the reactants and the products are to be noted down below their formulae.
3. Weight of the substance to be determined is to be calculated with the help of the ratio of the weights shown in the equation and the data given.

4. The same unit is to be used throughout the process of calculation.

Besides, one should remember—

$$(a) \text{ Density} = \frac{\text{mass}}{\text{volume}} \text{ i.e. } = \frac{m}{v}$$

$$(b) \text{ Specific gravity} = \frac{\text{mass of the substance}}{\text{mass of same vol. of water (at } 4^{\circ}\text{C)}}$$

$$(c) \text{ Weight of a substance} = (\text{sp. gr.} \times \text{vol.}) \text{ gm.}$$

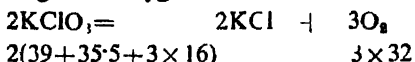
(d) Percentage of purity in case of a solid substance is expressed in terms of weight.

Thus, when 100 parts by weight of a solid contain 90 parts by weight of it in the pure state, the solid is said to be 90% pure.

Examples

Calculations based on direct weights :

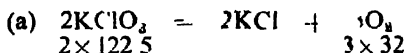
(1) How much potassium chlorate will be just required to produce 5 gms of oxygen ? (K=39, Cl=35.5)



From the chemical equation,

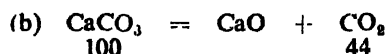
$$\begin{array}{rcl} 96 \text{ gms. of oxygen are produced from } 245 \text{ gms of KClO}_3, \\ \therefore 5 \text{ " " " " " " } \therefore \frac{245 \times 5}{96} \\ \text{or } 12.76 \text{ gms. of KClO}_3 \end{array}$$

(2) What loss in weight will be observed on heating sufficiently 1 gm. each of (a) potassium chlorate (b) calcium carbonate and (c) lead nitrate.



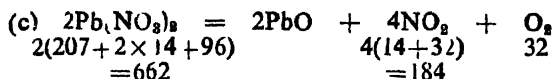
Here, loss in weight will be observed due to escape of gaseous oxygen.

$$\begin{array}{rcl} 245 \text{ gms of KClO}_3 \text{ will loose } 96 \text{ gms in weight} \\ \therefore 1 \text{ gm " " " " } \therefore \frac{96}{245} \text{ or } 0.39 \text{ gm. in wt.} \end{array}$$



The loss in weight is due to escape of carbon dioxide

$$\begin{array}{rcl} 100 \text{ gms of CaCO}_3 \text{ will lose } 44 \text{ gms in weight} \\ \therefore 1 \text{ gm. " " " " } \therefore \frac{44}{100} \text{ or } 0.44 \text{ gm} \end{array}$$



Here, the loss in wt. is due to escape of the gases *i.e.* nitrogen dioxide and oxygen.

For 662 gms of $\text{Pb}(\text{NO}_3)_2$, the loss in wt is $(184 + 32)$

or 216 gms

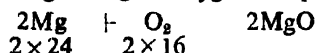
" 1 gm. " " " " " " $\frac{216}{662}$ or 0.32 gm

(3) 1 gm of magnesium is burnt in a closed vessel which contains 0.5 gm of oxygen.

(i) Which reactant is left in excess

(ii) Find the weight of the excess reagent.

Burning of Mg in oxygen is represented by the following equation



\therefore 48 gms of Mg requires 32 gms of oxygen for complete combustion

\therefore 1 gm of Mg requires $\frac{32}{48}$ or 0.67 gms of oxygen. As only 0.5 gm of oxygen is present in the vessel, a portion of Mg will be left in excess.

Now, 0.667 gm of oxygen is required for burning 1 gm of Mg

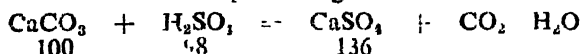
\therefore 0.5 " " " " " " " " $\frac{0.5}{0.667}$

0.75 gm of Mg (approx).

\therefore $(1 - 0.75)$ or 0.25 gm of Mg will remain unreacted.

(4) Find the weight of calcium sulphate formed by reacting 10 gms of chalk with same amount of H_2SO_4 .

The chemical reaction representing the formation of CaSO_4 is



100 gms of CaCO_3 react with 98 gms of sulphuric acid

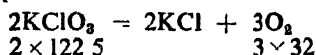
" 10 " " " " " $\frac{98 \times 10}{100}$ or 9.8 " "

The above result shows that CaCO_3 will react completely and $(10 - 9.8)$ or 0.2 gm of H_2SO_4 will remain unused.

100 gms of CaCO_3 will form 136 gms of CaSO_4

\therefore 10 " " " " " " $\frac{136 \times 10}{100}$ or 13.6 gm of CaSO_4 .

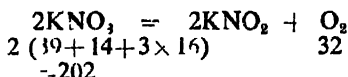
(5) What weight of potassium nitrate will give on heating as much oxygen as can be obtained by thermal decomposition of 20 gms of potassium chlorate?



245 gms of potassium chlorate will give 96 gms of oxygen

$$\therefore 20 \quad " \quad " \quad " \quad " \quad " \quad " \quad " \quad \frac{96 \times 20}{245} \quad \text{or } 7.84 \text{ gms}$$

of oxygen.



32 gms of oxygen are produced from 202 gms of KNO_3

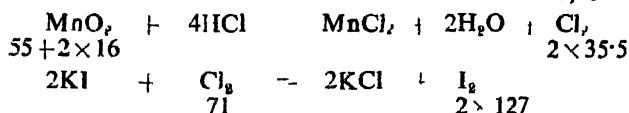
$$\therefore 7.84 \quad " \quad " \quad " \quad " \quad " \quad " \quad " \quad \frac{202 \times 7.84}{32}$$

or 49.49 gms of KNO_3

Calculations involving reactions taking place in succession.

(6) 16 gms of pure manganese dioxide is heated with excess of hydrochloric acid and the gas evolved is passed into a solution of potassium iodide. Calculate the weight of iodine that is liberated.

(Mn = 55, Cl = 35.5, I = 127)



From the above equations, it is evident that 87 gms of manganese dioxide react with hydrochloric acid to produce 71 gms of chlorine which react with potassium iodide to liberate 254 gms of iodine.

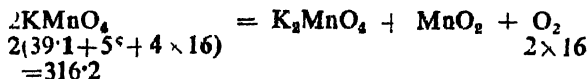
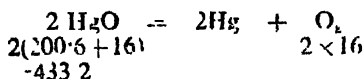
Chlorine produced from 87 gms of MnO_2 liberates 254 gms of iodine.

\therefore Chlorine produced from 16 gms of MnO_2 liberates

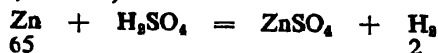
$$\frac{254 \times 16}{87} \quad \text{or } 46.71 \text{ gms of Iodine}$$

(7) What weight of potassium permanganate of 6% purity will yield on heating as much oxygen as can be obtained by thermal decomposition of 4.332 gms of mercuric oxide?

(K = 39, Mn = 55, Hg = 200.6)



Find out the weight and composition of the residue in each case.
(Cu=63, Zn=65)



65 gms of zinc yield 2 gms of hydrogen

$$\therefore 13 \text{ " " " " } \frac{2 \times 13}{65} \text{ or, } 0.4 \text{ gm of hydrogen}$$



2 gms of H_2 reduce completely 79 gms of CuO

$$\therefore 0.4 \text{ " " " " reduces " } \frac{79 \times 0.4}{2} \text{ or, } 15.8 \text{ gms of CuO}$$

Again, 2 gms of H_2 produce 63 gms of copper

$$\therefore 0.4 \text{ " " " " " } \frac{63 \times 0.4}{2} \text{ or, } 12.6 \text{ gms of Cu.}$$

(a) In the first case, the hydrogen evolved reduces completely the cupric oxide (10 gms) to produce metallic copper.

79 gms of CuO on being reduced give 63 gms of Cu

$$\therefore 10 \text{ " " " " " " " } \frac{63 \times 10}{79} \text{ or, } 7.97 \text{ gms of copper}$$

\therefore Only 7.97 gms of copper are left as residue.

(b) In the second case, the hydrogen evolved can partly reduce CuO (20 gms). So the residue will be a mixture of CuO and Cu .

As shown above, 0.4 gms of hydrogen reacts with 15.8 gms of CuO .

$$\therefore \text{wt. of unreacted CuO} = 20 - 15.8 = 4.2 \text{ gms.}$$

Again, 12.6 gms of copper are produced through reduction of 15.8 gms of cupric oxide by 0.4 gms of hydrogen.

$$\therefore \text{The residue} = 4.2 \text{ gms of CuO} + 12.6 \text{ gms of copper}$$

$$\therefore \text{wt. of the residue} = 4.2 + 12.6 = 16.8 \text{ gms.}$$

(10) A sample of coal contains 85% of carbon, 5% of hydrogen and 10% of oxygen. 1.5 gm. of this coal is completely burnt in a current of CO_2 -free air and the resulting products are successively passed through two weighed U-tubes joined together and filled respectively with anhydrous CaCl_2 and soda lime. Calculate the alteration in the weights of the tubes.

When coal is burnt in air, CO_2 and steam are produced. The U-tubes containing the anhydrous calcium chloride and soda lime gain in weight due to absorption of steam and CO_2 in them respectively.

100 gms of coal contain 85 gms. of carbon

$$\therefore 1.5 \text{ " " " " } \frac{85 \times 1.5}{100} \text{ or, 1.275 gms of carbon}$$

100 " " " " 5 gms of hydrogen

$$\therefore 1.5 \text{ " " " " } \frac{5 \times 1.5}{100} \text{ or, 0.075 gm of hydrogen.}$$



4 gms of hydrogen yield 36 gms of steam

$$\therefore 0.075 \text{ gm " " } \frac{36 \times 0.075}{4} \text{ or, 0.675 gm of steam}$$

\therefore Increase in wt. of CaCl_2 -tube = 0.675 gms.



12 gms of carbon evolve 44 gms of CO_2

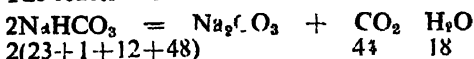
$$\therefore 1.275 \text{ " " " " } \frac{44 \times 1.275}{12} \text{ or, 4.675 gms of CO}_2$$

\therefore wt. of soda lime tube increases by 4.675 gms.

Analysis of mixtures :

(11) 3.0 gms of a mixture of anhydrous sodium carbonate and sodium bicarbonate lose 0.348 gms in wt. on heating. Calculate the percentage of anhydrous sodium carbonate in the mixture.

The reaction involved is



The loss in wt is due to escape of carbon dioxide and steam from NaHCO_3 . Na_2CO_3 will remain unaffected on heating..

Where the loss is (44+18) or, 62 gms, the wt. of NaHCO_3 is 168 gms.

$$\therefore \text{ " " " is 0.348 gm. the wt of NaHCO}_3 \text{ is } \frac{168 \times 0.348}{62} \text{ gm}$$

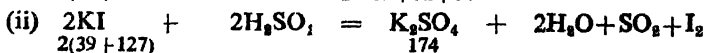
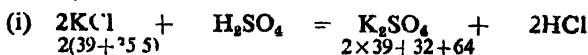
= 0.943 gm.

So, 3 gms of the mixture contain (3.0-0.943)=2.057 gms of Na_2CO_3

$$\therefore \% \text{ of Na}_2\text{CO}_3 \text{ in the mixture} = \frac{2.057 \times 100}{3} = 68.56$$

(12) A mixture of KCl and KI was converted to K_2SO_4 . The weight of sulphate produced was found to be equal to the weight of the mixture originally taken. Find the percentage composition of the mixture. ($\text{K}=39$; $\text{Cl}=35.5$, $\text{I}=127$)

Let 1 gm of the mixture contain x gm of KCl. Then the weight of KI in the mixture is $(1-x)$ gm. The chemical reactions taking place are :



Then,

149 gms of KCl produce 174 gms of K_2SO_4

$$\therefore x \quad \text{,,} \quad \text{,,} \quad \frac{174}{149} x \text{ gms. ,}$$

Again 332 gms of KI produce 174 gms of K_2SO_4

$$\therefore (1-x) \text{ gm} \quad \text{,,} \quad \text{produces} \quad \frac{174 \times (1-x)}{332} \text{ gms of } K_2SO_4$$

But potassium sulphate formed is equal to the weight of the original mixture

$$\frac{174x}{149} + \frac{174}{332} \times (1-x) = 1$$

Or, $x = 0.7394$ gm = wt of KCl.

\therefore of KCl in the mixture $0.7394 \times 100 = 73.94$

\therefore of KI in the mixture $= (100 - 73.94)$ or, 26.06. So, the mixture contains 73.94% KCl and 26.06% KI.

(13) 1.873 gms of a mixture of sodium and potassium chloride gave with silver nitrate 3.731 gms of silver chloride. Find out the amount of sodium chloride in the mixture. ($K=39$, $Ag=108$)

Let the wt. of NaCl in the mixture be x gm

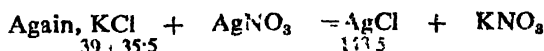
and ,, ,, ,, KCl ,, ,, ,, $(1.873-x)$ gm

The chemical reaction shows :



58.5 gms of NaCl produce 143.5 gms of AgCl

$$\therefore x \text{ gm} \quad \text{,,} \quad \text{,,} \quad \frac{143.5}{58.5} \times x \text{ or } 2.453x \text{ gm of AgCl}$$



\therefore 74.5 gms of KCl produce 143.5 gms of AgCl

$$\therefore (1.873-x) \text{ ,,} \quad \text{,,} \quad \frac{143.5 \times (1.873-x)}{74.5} \text{ gm.}$$

Or $(3.61 - 1.926x)$ gm AgCl

$$\therefore 2.453x + 3.61 - 1.926x = 3.731$$

$$\therefore x = 0.229 \text{ gm} = \text{Amount of NaCl}$$

(14) A mixture of FeO and Fe_3O_4 when heated in air to a constant weight gains, 5% in weight. Find the composition of the initial mixture. ($\text{Fe}=55.8$)

Let us suppose that 100 gms. of the said mixture contains x gms. of FeO and $(100-x)$ gms of Fe_3O_4 .

When heated in air, the FeO fraction is converted into Fe_2O_3 and gains in weight and Fe_3O_4 fraction remains unaltered.



According to the above equation, $4(55.8+16)$ gms of FeO are converted to $2(2 \times 55.8 + 48)$ gms of Fe_2O_3

i.e., 4×71.8 gms FeO are converted into
 2×159.6 gms. Fe_2O_3 .

$\therefore x$ gm FeO is converted into

$$\frac{2 \times 159.6 \times x}{4 \times 71.8} \text{ gms. } \text{Fe}_2\text{O}_3 = \frac{159.6x}{143.6} \text{ gm } \text{Fe}_2\text{O}_3$$

It is given that the mixture gains 5% in weight. So, after heating 100 gms. of the mixture in air to constant weight, we get,

$$\frac{159.6x}{143.6} + (100 - x) = 105.$$

$$\therefore 16x = 5 \times 143.6$$

$$x = \frac{5 \times 143.6}{16} = 44.875 \text{ gms.}$$

Hence, the mixture contains 44.875 FeO and 55.125% Fe_3O_4 .

Miscellaneous type :

(15) A sample of metallic zinc contains a little impurity which is inert to HCl. 10 gms of the sample of the metal react completely with 30.1 cc. of hydrochloric acid of sp. gr. 1.18. If this hydrochloric acid contains 30% HCl by weight, calculate the percentage of metal in the sample. ($\text{Zn}=65.38$)

Given sp. gr. of acid = 1.18

\therefore wt of l.c.c of hydrochloric acid = 1.18 gms

wt of 30.1 c.c. „ „ „ = $1.18 \times 30.1 = 35.518$ gms

100 gms of the acid contain 30 gms of pure acid

$$\therefore 35.518 \text{ „ „ „ } \frac{30 \times 35.518}{100} = 10.6554 \text{ gms of acid}$$



∴ 73 gms of hydrochloric acid react with 65.38 gms of Zn

∴ 10.6554 " " " " " $\frac{65.38 \times 10.6554}{73}$

Or 9.54 gms of zinc.

But as per question, 10 gms of zinc react with 30 l.c.c. of hydrochloric acid.

∴ 10 gms of the impure sample contain 9.54 gms of pure zinc

∴ 100 " " " " " " " 95.4 " " " "

∴ % of the metal = 95.4

Chemical calculations from equations involving weights and volumes.

To work out such calculations, the correct equation representing the chemical reaction is to be written first. The relative weights of the substances taking part in the reaction can be obtained from the equation as described earlier. The quantities of the reacting gaseous substances or those of the products are to be expressed in volumes while the quantities of the solid or liquid must be expressed in weights. Further, it is important to remember—
(1) The equation expresses the condition of reaction at N.T.P. i.e. at the temperature of 0°C and pressure of 760 mm.

(2) The volume of a gas under any temperature and pressure is converted to that it would occupy at N.T.P. by applying the

gas equation $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$.

(3) One gm-molecule of a substance in the gaseous state occupies a volume of 22.4 litres at N.T.P. and vice versa. It is customary to express the actual volume of a gas in litres or in c.c. (m.l.)

(4) At N.T.P. weight of 1 litre of hydrogen = 0.089 ≈ 0.09 gm.

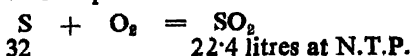
(5) Weight of 1 litre of a gas at N.T.P. = Density of the gas × 0.09

(6) Vapour density = $\frac{\text{wt of a certain vol of a gas}}{\text{wt of same vol of hydrogen}}$
(under same temp. and pressure)

(7) Vapour density × 2 = Mol. wt.

Examples :

(1) What weight of sulphur must be burnt in air so as to yield 10 litres of sulphur dioxide at N.T.P. ?



It is evident from the above equation,

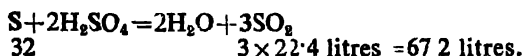
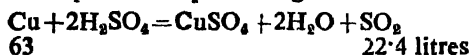
22.4 litres of SO_2 are produced by burning 32 gms of S

$$\therefore 10 \text{ " " " " " " } \frac{32 \times 10}{22.4}$$

or 14.286 gms of sulphur.

(2) 10 gms of copper and 10 gms of sulphur are separately heated with conc. sulphuric acid. Find the ratio of the volumes of sulphur dioxide evolved. ($\text{Cu}=63$, $\text{S}=32$).

The equations representing the reactions are :



At N.T.P.,

63 gms of copper yield 22.4 litres of SO_2

$$\therefore 10 \text{ " " " " " " } \frac{22.4 \times 10}{63}$$

Again, 32 gms of sulphur yield 67.2 litres of SO_2

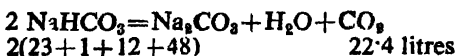
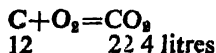
$$\therefore 10 \text{ " " " " " " } \frac{67.2 \times 10}{32}$$

$$\therefore \frac{\text{Vol. of } \text{SO}_2 \text{ produced from copper and acid}}{\text{Vol. of } \text{SO}_2 \text{ produced from sulphur and acid}} = \frac{22.4 \times 10}{63} \div \frac{67.2 \times 10}{32} = \frac{32}{189}$$

\therefore Ratio of vols. of SO_2 is 32 : 189

(3) Carbon dioxide can be prepared by burning carbon in oxygen or by heating sodium bicarbonate. What weight of carbon or sodium bicarbonate will be required to produce 33.6 litres of carbon dioxide in each case.

The reactions involved are :



Now 22.4 litres of CO_2 are produced by burning 12 gms of carbon

$$\therefore 33.6 \text{ " " " " " " " " } \frac{12 \times 33.6}{22.4}$$

or 18 gms of Carbon.

Again, 22.4 litres of CO_2 are produced by heating 168 gms of NaHCO_3

$$33.6 \quad , \quad , \quad , \quad , \quad , \quad , \quad \frac{168 \times 33.6}{22.4}$$

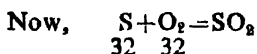
or 252 gms of NaHCO_3

(4) Air contains 21% of oxygen by volume. What volume of air will be required to burn completely 1000 gms of sulphur containing 4% non-combustible matter?

100 gms of sulphur contain 4.0 gms of non-combustible matter

\therefore 1000 „ „ „ „ 40 gms „ „ „

\therefore Wt. of sulphur to be burnt = $1000 - 40 = 960$ gms.



It is evident from the above equation,

32 gms of sulphur combine with 32 gms of oxygen

$$\therefore 960 \quad , \quad , \quad , \quad , \quad , \quad \frac{32 \times 960}{32}$$

or 960 gms of oxygen

32 gms of oxygen at N.T.P. occupy 22.4 litres

$$\therefore 960 \quad , \quad , \quad , \quad , \quad , \quad \frac{960 \times 22.4}{32} \text{ or } 672 \text{ litres}$$

As per data given,

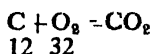
21 litres of oxygen are present in 100 litres of air

$$\therefore 672 \quad , \quad , \quad , \quad , \quad , \quad \frac{100 \times 672}{21}$$

or 3200 litres of air.

\therefore Vol. of air required is 3200 litres.

(5) How many litres of air containing 23% of oxygen by weight would be necessary to burn 17.25 gms of pure carbon to carbon dioxide. [Density of air (H-1) is 1.4; at N.T.P., 1 litre of hydrogen weighs 0.09 gm]



It is evident from the above equation,

12 gms of carbon combine with 32 gms of oxygen

$$\therefore 17.25 \quad , \quad , \quad , \quad , \quad , \quad \frac{32 \times 17.25}{12}$$

or 46 gms of oxygen

As per data supplied,

23 gms of oxygen are present in 100 gms of air

$$\therefore 46 \text{ ,, ,, ,, ,, ,, } \frac{46 \times 100}{23} \text{ or 200 gms of air}$$

Density of air = 14.4 ; at N.T.P., wt of 1 litre of hydrogen = 0.09 gm

$$\therefore \text{ At N.T.P., wt of 1 litre of air} = 14.4 \times 0.09 = 1.296 \text{ gms}$$

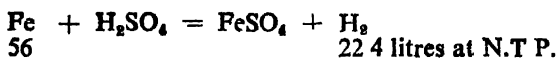
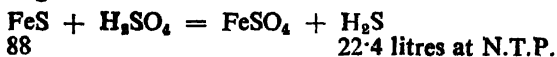
i.e., at N.T.P., 1.296 gms of air occupy 1 litre

$$\therefore \text{ ,, ,, 200 ,, ,, ,, } \frac{200}{1.296} \text{ or 154.34 litres.}$$

$$\therefore \text{ Vol. of air required} = 154.34 \text{ litres.}$$

(6) Hydrogen sulphide produced by the action of dil. sulphuric acid on a sample of ferrous sulphide was found to contain 9% (by volume) of hydrogen as impurity. Calculate the percentage of iron in the sample. (Fe = 56, S = 32)

It is evident from the question that the impurity present in ferrous sulphide is iron which reacts with the dil acid to liberate hydrogen.



Considering 22.4 litres of hydrogen as 9%, the vol. of the residual 91% $\text{H}_2\text{S} = \frac{22.4 \times 91}{9}$ litres.

Now, 22.4 litres of H_2S are obtained from 88 gms of FeS

$$\therefore \frac{22.4 \times 91}{9} \text{ ,, ,, ,, } \frac{88 \times 22.4 \times 91}{22.4 \times 9} \text{ gms.}$$

or, 889.78 gms of FeS.

$$\therefore \text{ Total weight of the mixture} = 889.78 + 56 = 945.78 \text{ gms}$$

945.78 gms of the mixture contain 56 gms of Fe

$$\therefore 100 \text{ ,, ,, ,, } \frac{56 \times 100}{945.78} \text{ or } 5.92 \text{ gms of Fe}$$

$$\therefore \text{ The sample contains } 5.92\% \text{ of iron.}$$

(7) 2730 c.c. of a gas mixture contain 20% of methane, 60% of carbon monoxide, and 20% of hydrogen.

What weight of KClO_3 will be required to generate just sufficient oxygen to oxidise completely the gas mixture ?

As per given data.

100 c.c. of the mixture contain 20 c.c. of methane

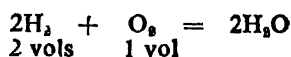
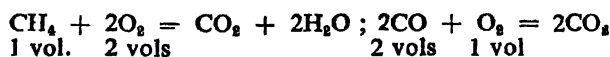
$$\therefore 2730 \text{ ,, ,, ,, ,, } \frac{20 \times 2730}{100} \text{ or, 546 c.c. of methane}$$

100 c.c. of the mixture contain 60 c.c. of carbon monoxide

$$\therefore 2730 \text{ ,, ,, ,, ,, } \frac{60 \times 2730}{100} \text{ or, 1638 c.c. of CO.}$$

100 ,, ,, ,, ,, 20 c.c. of hydrogen

$$\therefore 2730 \text{ ,, ,, ,, ,, } 546 \text{ ,, ,, }$$



From the above equations, it is evident that

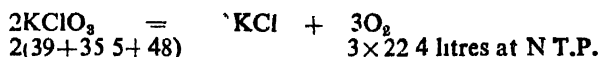
546 c.c. of methane are oxidised by 1092 c.c. of oxygen

1638 ,, ,, carbon monoxide ,, ,, 819 ,, ,, ,,

546 ,, ,, hydrogen ,, ,, 273 ,, ,, ,,

So total vol. of oxygen required at N.T.P.

$$= 1092 + 819 + 273 = 2184 \text{ c.c.} = 2.184 \text{ litres}$$



67.2 litres of oxygen are obtained from 245 gms of KClO_3

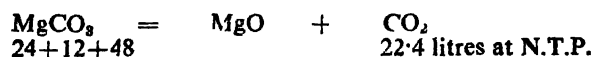
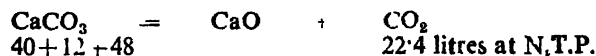
$$\therefore 2184 \text{ ,, ,, ,, ,, } \frac{245 \times 2.184}{67.2} \text{ or, 7.96 gms of } \text{KClO}_3$$

(8) 1 gm of a mixture of CaCO_3 and MgCO_3 gives on ignition 240 c.c. of CO_2 at N.T.P. Calculate the composition of the mixture.

Let the weight of CaCO_3 in the mixture = x gm.

$$\therefore \text{ ,, ,, ,, } \text{MgCO}_3 \text{ ,, ,, } (1-x) \text{ gm.}$$

The chemical reactions involved are .



At N.T.P. 100 gms of CaCO_3 produce 22.4 litres of CO_2

$$\therefore x \text{ ,, ,, ,, } \frac{22.4 \times x}{100} \text{ litres of } \text{CO}_2$$

Again, 84 gms of MgCO_3 produce 22.4 litres of CO_2

$$\therefore (1-x) \quad , \quad , \quad \frac{22.4(1-x)}{84} \text{ litres of } \text{CO}_2$$

Now, according to the data given,

$$\frac{22.4x}{100} + \frac{22.4(1-x)}{84} = 240 \text{ c.c.} = 0.24 \text{ litres}$$

$$\text{or, } \frac{5.6x}{25} + \frac{5.6(1-x)}{21} = 0.24 \quad \text{or, } \frac{117.6x + 140 - 140x}{525} = 0.24$$

$$\text{or, } -22.4x = 126 - 140 = -14 \quad \text{or, } x = 0.625$$

\therefore Wt of CaCO_3 in 1 gm of the mixture = 0.625 gm.

\therefore % CaCO_3 in the mixture = 62.5

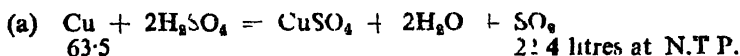
Again, wt of MgCO_3 in 1 gm of the mixture = $1 - 0.625$
 $= 0.375 \text{ gm}$

\therefore % MgCO_3 in the mixture = 37.5

So the mixture contains 62.5% of CaCO_3 and 37.5% of MgCO_3 .

In solving the following problems, the gas laws equation described in Chapter 8 has been applied

(i) (a) What weight of copper must be heated with conc. sulphuric acid to produce 500 c.c. of sulphur dioxide at 27°C and 750 mm. pressure? (b) What volume of H_2S at N.T.P. will be required to precipitate copper in the solution? (c) How much ferrous sulphide will give the requisite quantity of sulphuretted hydrogen? ($\text{Cu} = 63.5$, $\text{Fe} = 56$)



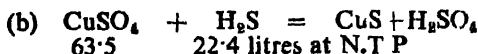
Let the vol. occupied by 500 c.c. of SO_2 at N.T.P be V_1 . Then applying the combined gas laws equation $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ we get.

$$\frac{760 \times V_1}{273} = \frac{750 \times 500}{273 + 27} \quad \text{or } V_1 = 449 \text{ c.c. or } 0.449 \text{ litre.}$$

22.4 litres of SO_2 are produced from 63.5 gms of copper

$$\therefore 0.449 \quad , \quad , \quad , \quad , \quad , \quad , \quad \frac{63.5 \times 0.449}{22.4} \text{ gms}$$

or 1.2728 gms of copper.



At N.T.P., 63.5 gms of copper are precipitated by 22.4 litres of H_2S

$$\therefore 1.2728 \quad , \quad , \quad , \quad , \quad , \quad \frac{22.4 \times 1.2728}{63.5}$$

or 0.449 litres of H_2S



22.4 litres of H_2S are produced from 88 gms of FeS

$$\therefore 0.4489 \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \frac{88 \times 0.4489}{22.4}$$

or 1.76 gms of FeS

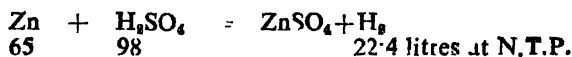
(10) A sample of dil. sulphuric acid contains 65% of acid by weight and the density of the acid is 1.55. What volume of hydrogen at 27°C and 750 mm will be evolved when 750 gms of zinc are made to react with 1 litre of the above acid? ($\text{Zn}=65$)

Wt of 1 litre of the acid = $1000 \times 1.55 = 1550$ gms.

From the given data,

100 gms of the acid contain 65 gms of acid

$$\therefore 1550 \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \frac{65 \times 1550}{100} \quad \text{or } 1007.5 \text{ gms of acid.}$$



98 gms of H_2SO_4 react with 65 gms of Zn

$$1007.5 \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \frac{65 \times 1007.5}{98} \quad \text{or } 663.24 \text{ gms of Zn}$$

But amount of zinc added = 750 gms

\therefore In the reaction, all the acid has been converted to sulphate.

At N.T.P. 98 gms of H_2SO_4 produce 22.4 litres of H_2

$$\therefore \text{,,} \quad 1007.5 \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \frac{22.4 \times 1007.5}{98} \quad \text{or } 230.3 \text{ litres of } \text{H}_2$$

Let V_2 be the vol. occupied by hydrogen at 27°C and 750 mm.

By applying the gas laws equation $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$, we get,

$$\frac{760 \times 230.3}{273} = \frac{V_2 \times 750}{273 + 27} \quad \text{or} \quad V_2 = \frac{760 \times 230.3 \times 300}{750 \times 273}$$

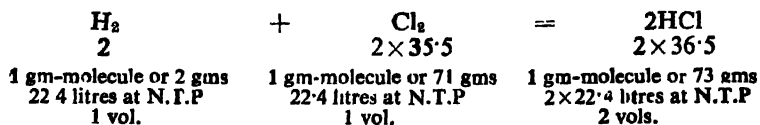
or 256.4 litres.

Chemical calculations from equations involving volume and volume.

Eudiometry : The term eudiometry refers to various types of chemical calculations based on the volumes of gases taking part in gaseous reactions. Such reactions are generally carried out in an eudiometer tube, a specially devised apparatus meant for measuring

the volumes of the gases. Two relationships derived from the Gay Lussac's law of gaseous volumes and Avogadro's hypothesis form the basis of eudiometric calculations. These are—

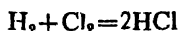
(i) In gaseous reactions, the simple volume ratio of various reactants and the products is also the molecular ratio and vice versa. (ii) At N.T.P., the molar volume of any gas is 22.4 litres.



The above equation shows—

1 molecule of hydrogen + 1 molecule of chlorine = 2 molecules of hydrogen chloride
 or, 1 gm-molecule of „ + 1 gm-molecule of chlorine = 2 gm-molecules of hydrogen chloride
 or, 1 ml of „ + 1 ml of chlorine = 2 ml of hydrogen chloride
 or, 50 ml „ + 50 ml „ = 100 ml of hydrogen chloride

So, in a gaseous reaction, the ratio of the molecules and that of the volumes of the gaseous substances are the same.

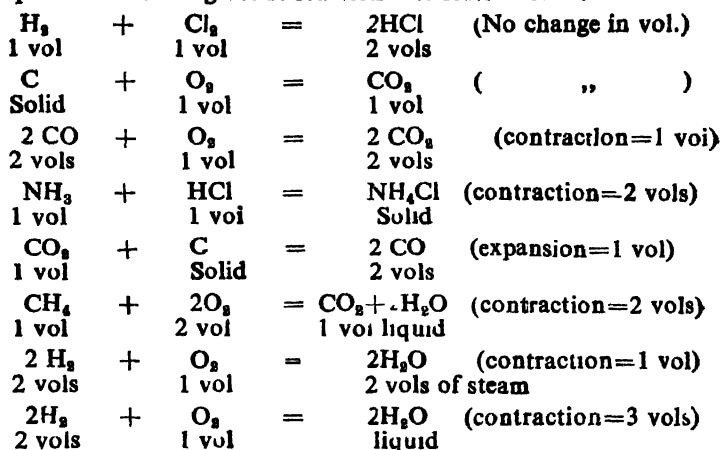


	Hydrogen	: Chlorine	: Hydrogen chloride
Ratio of molecules	1	:	2
Ratio of volumes	1	:	2
Similarly in $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$			
	Nitrogen	: Hydrogen	: Ammonia
Ratio of molecules	1	:	2
Ratio of volumes	1	:	2

Now, from a balanced chemical equation representing a gaseous reaction, we can get the number of molecules (moles) as well as the volumes of the substances taking part in the reaction and it is possible to calculate either the volumes of the products from the given volumes of the reactants or the volumes of reactants required to produce the given volumes of the products.

N. B It is to be noted further that (i) in comparing the volumes of the gases involved in a reaction, 1 gm-molecule of a gas is assumed to occupy unit volume. In all other cases, the volume at N.T.P. (i.e. 22.4 litres) is taken. (ii) the equation represents the reaction at standard conditions i.e. at N.T.P. (iii) The volumes of solids or liquids formed during gaseous reactions are negligible in comparison to the volumes of the gases and in eudiometric calculations, a solid or liquid is considered to occupy no volume or zero volume.

Equations of some gaseous reactions are stated below.



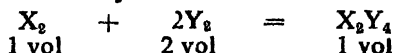
Whenever hydrogen and oxygen combine together to produce steam which on cooling condenses to water occupying negligible volume, there is a contraction in volume. One-third of the contraction will represent the volume of oxygen and the two-thirds will represent the volume of hydrogen taking part in chemical combination.

Sometimes, a gas present in a mixture of gases is absorbed by using a suitable absorbent. As a result, the total volume of the mixture is reduced. So, it becomes easy to find out the volume of the gas absorbed by knowing the difference between the volumes of the mixture before and after addition of the absorbent. The names of some gases with their absorbents are given below.

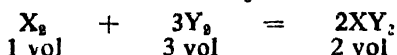
Gas	Absorbent
Oxygen, O_2	Alkaline pyrogallate solution
Ozone, O_3	Terpentine oil
Carbon dioxide CO_2 & sulphur dioxide SO_2	Caustic soda or caustic potash solution
Carbon monoxide CO & acetylene, C_2H_2	Ammoniacal cuprous chloride solution.
Nitric oxide, NO	Ferrous sulphate solution.
Ethylene, C_2H_4	Conc. sulphuric acid.

It may be stated here that when two elementary gases of known atomicity react with each other to give a gaseous product, then from the volume of each of the reacting gases and the product (all volumes being measured at the same temp. and pressure), the

molecular formula of the product can be found out. For example, if 1 litre of a diatomic gaseous element, X reacts with 2 litres of another diatomic elementary gas Y to form 1 litre of a gaseous compound, then the molecular formula of the product will be X_2Y_4 . This can easily be understood from the following equation.



If these elementary gases react in the proportion of 1 : 3 by volume to produce 2 vols of the gaseous compound, then compound will be of molecular formula XY_3 .

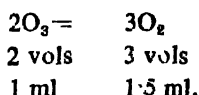


Numerical examples :

Calculations based on volumes of reacting gases :

(1) When 100 ml of a sample of ozonised oxygen are treated with terpentine, the volume is reduced to 70 ml. Another 100 ml of the same sample is heated till all the ozone decomposes, and then cooled to the original temperature and pressure. What volume will the gas occupy ?

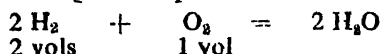
We know that ozone is absorbed by terpentine. So 100 ml. of ozonised oxygen will contain $(100 - 70) = 30$ ml. of ozone and 70 ml. of oxygen.



\therefore 30 ml of ozone on decomposition will produce 45 ml of oxygen

Hence total vol of the gas on cooling = $70 + 45 = 115$ ml.

(2) 20 c.c. of oxygen were mixed with 100 c.c. of hydrogen at N.T.P. and exploded. Calculate the volume of the residual gas when cooled to the original temperature.



2 c.c. of hydrogen combine with 1 c.c. of oxygen

40 „ „ „ „ „ 20 c.c. „ „

(at ordinary temperature, vol. occupied by water is negligible)

\therefore Vol of unused hydrogen or of residual gas = $(100 - 40)$ c.c.
60 c.c.

(3) Air contains 20% of oxygen by volume. What volume of air is required to produce 10 litres of carbon dioxide ?



So, 1 vol. of CO_2 requires for its production 1 vol. of O_2
 \therefore 10 litres „ require „ „ „ 10 litres of O_2

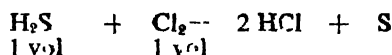
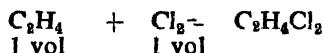
As per given data,

20 litres of oxygen are present in 100 litres of air

\therefore 10 „ „ „ „ „ „ 50 „ „ „

\therefore Required vol. of air = 40 litres

(4) What vol. of chlorine at N.T.P. would be required to
 (a) combine with 10 litres of ethylene and (b) to decompose 10
 litres of hydrogen sulphide?



It is evident from the above equations that both ethylene and hydrogen sulphide require their own volumes of chlorine for reaction.

\therefore 10 litres of ethylene will require 10 litres of chlorine and 10 litres of H_2S will also require 10 litres of chlorine.

(5) 50 c.c. of methane were mixed with 90 c.c. of oxygen and the mixture was exploded. Calculate the composition of the resulting gas mixture, the temperature and pressure remaining the same.



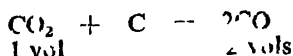
Now, 1 vol. of methane combines with 2 vols of oxygen to produce 1 vol of carbon dioxide

\therefore 45 c.c. of methane will combine with 90 c.c. of oxygen to produce 45 c.c. of carbon dioxide.

\therefore vol of unreacted methane = 10 - 45 = 5 c.c.

and „ „ CO_2 formed = 45 c.c.

(6) 750 c.c. of carbon dioxide are passed over red hot carbon. The volume becomes 1050 c.c. Find the composition of the products assuming that all the gases are measured at N.T.P.



From the above equation, it is clear that the vol. of carbon dioxide is doubled when it is passed over red hot carbon and CO_2 is converted to CO . In this case, only a part of CO_2 has been reduced to CO

Let x c.c. of CO_2 has been reduced by carbon to produce CO .

Then, vol. of CO formed = $2x$ c.c.

Vol. of CO_2 unreduced = $(750 - x)$ c.c.

$\therefore (750 - x) + 2x = 1050 \quad \therefore x = 300$

Hence vol of carbon monoxide formed = $2 \times 300 = 600$ c.c.

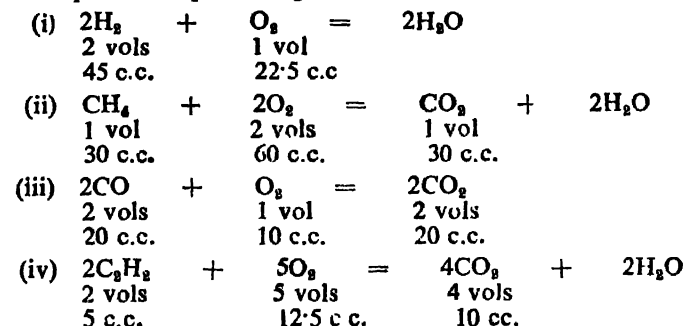
\therefore After the reaction, the gas mixture will contain

$750 - 300 = 450$ c.c. of CO_2 and 600 c.c. of carbon monoxide.

Composition of the gas mixtures :

(7) A sample of coal gas contained 45% H_2 , 30% CH_4 , 20% CO and 5% C_2H_2 . 100 c.c. of the gas were mixed with 160 c.c. of oxygen and exploded. Calculate the volume and composition of the resulting mixture when cooled to the original temperature.

The equations representing the combustions are—



At ordinary temperature, the volume occupied by water is negligible.

So the resulting gas mixture will contain carbon dioxide and unreacted oxygen

	Vol of the gas	Oxygen used	Vol. of CO_2 formed
(i)	Hydrogen, 45 c.c.	22.5 c.c.
(ii)	Methane, 30 c.c.	60 c.c.	30 c.c.
(iii)	Carbon monoxide 20 c.c.	10 c.c.	20 c.c.
(iv)	Acetylene, 5 c.c.	12.5 c.c.	10 c.c.
	Total	105.00 c.c.	Total 60 c.c.

\therefore Oxygen left unused = $(160 - 105.0) = 55$ c.c.

Carbon dioxide formed = 60 c.c.

Total vol. of the residual mixture = $(55 + 60) = 115$ c.c.

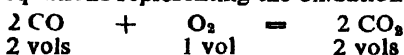
(8) 10 c.c. of a mixture of carbon monoxide, methane and ethane were mixed with 40 c.c. of oxygen and the mixture was then exploded. After cooling, the residual gases were found to consist of 12 c.c. of carbon dioxide and 23 c.c. of unused oxygen. What was the composition of the gas mixture?

Let the vol. of carbon monoxide in the mixture = x c.c.

vol of methane = y c.c. and vol of ethane = z c.c.

$\therefore x + y + z = 10$ c.c.

The equations representing the oxidation are—



vol of gas	vol of O_2 used	vol of CO_2 formed
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Carbon monoxide, x c.c.	$\frac{x}{2}$ c.c.	x c.c.
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Methane, y c.c.	$2y$ c.c.	y c.c.
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Ethane, z c.c.	($\frac{7}{2}$) z c.c.	$2z$ c.c.
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$\therefore x + y + z = 10$

$$\frac{x}{2} + 2y + \frac{7}{2}z = 40 - 23 = 17$$

$$x + y + 2z = 12$$

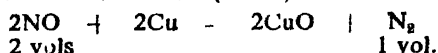
On solving, $x = 4$ c.c. ; $y = 4$ c.c. ; $z = 2$ c.c.

9. 50 c.c. of a mixture of nitrogen and nitric oxide are passed over ignited copper and the gaseous products are collected and found to occupy 40 c.c. Calculate the percentage composition of the mixture.

Total vol of N_2 and $\text{NO} = 50$ c.c.

Let the vol. of N_2 be x c.c.

Then the vol. of $\text{NO} = (50 - x)$ c.c.



From the above equation 2 vols of nitric oxide produce 1 vol of nitrogen.

$\therefore (50 - x)$ c.c. of nitric oxide produce $\frac{50 - x}{2}$ c.c. of nitrogen

$$\therefore x + \frac{50 - x}{2} = 40$$

$\therefore x = 30$ c.c. or vol of nitrogen

$(50 - 30) = 20$ c.c. or vol of nitric oxide.

$$\% \text{ of nitrogen by volume} = \frac{30 \times 100}{50} = 60$$

$$\% \text{ „ nitric oxide „} = \frac{20 \times 100}{50} = 40$$

\therefore The mixture contains 60% of nitrogen and 40% of nitric oxide.

(10) 29 c.c. of a mixture of CO_2 , H_2 , N_2 and O_2 at N.T.P. decreases to 21 c.c. when shaken with KOH . A further contraction of 15 c.c. is observed when an electric spark is passed through the remaining gas; but there is no further contraction when the residual gas is shaken with alkaline pyrogallate. Calculate the percentage composition by volume of the original mixture.

CO_2 is absorbed by KOH

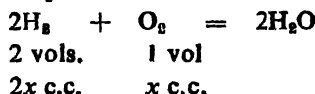
$$\therefore \text{vol. of } \text{CO}_2 = (29 - 21) = 8 \text{ c.c.}$$

$$\therefore \text{ " " " percent} = \frac{8 \times 100}{29} = 27.58\%$$

As a result of combustion, the total vol. of O_2 is used up as the residual gas does not suffer any contraction when shaken with alkaline pyrogallate.

Moreover, as per given data, the residual gas does not contain hydrogen i.e. the residual gas consists of nitrogen only. The contraction observed on explosion is due to the combination of oxygen and hydrogen forming water which occupies negligible volume.

Let the vol. of O_2 be x c.c.



$$\therefore 2x + x = 15 \quad \therefore x = 5 \text{ c.c.} = \text{vol of } \text{O}_2$$

$$\therefore \text{ vol. of } \text{O}_2 \text{ percent} = \frac{5 \times 100}{29} = 17.24\%$$

$$\text{vol. of } \text{H}_2 = x \times 2 = (5 - 5) = 10 \text{ c.c.}$$

$$\text{Hence vol. of } \text{H}_2 \text{ percent} = \frac{10 \times 100}{29} = 34.48\%$$

$$\begin{aligned} \text{vol. of nitrogen or the residual gas} &= 29 \text{ c.c.} - (8 + 5 + 10) \text{ c.c.} \\ &= 6 \text{ c.c.} \end{aligned}$$

$$\therefore \text{ vol. of nitrogen percent} = \frac{6 \times 100}{29} = 20.69\%$$

Determination of molecular formula of a gas :

(11) At N.T.P., 20 c.c. of nitrogen dioxide when passed over heated copper yield 10 c.c. of nitrogen. The vapour density of the oxide is found to be 23. What is the molecular formula of the oxide?

Let the mol. formula of the oxide N_xO_y

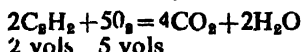


20 c.c.

10 c.c.

Let V_1 be the vol. of acetylene at N.T.P. Applying the gas equation, $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$, we get

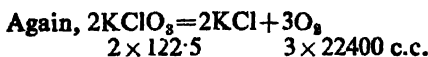
$$\frac{760 \times V_1}{273} = \frac{750 \times 152}{273 + 27} \quad \text{or} \quad V_1 = 136.5 \text{ c.c.}$$



It is found from the above equation,

2 c.c. of acetylene for its combustion require 5 c.c. of O_2

$$\therefore 136.5 \text{ c.c.} \quad \text{ " " " " " " } \quad \frac{5 \times 136.5}{2} \quad \text{or} \quad 341.25 \text{ c.c. of } \text{O}_2$$



3×22400 c.c. of oxygen are prepared from 245 gms of KClO_3

$$\therefore 341.25 \quad \text{ " " " " " " } \quad \frac{2.5 \times 341.25}{3 \times 22400} \quad \text{or} \quad 1.244 \text{ gms of } \text{KClO}_3$$

$$\% \text{ of } \text{KClO}_3 \text{ in the sample} = \frac{1.244 \times 100}{1.555} = 80$$

\therefore The sample contains 80% KClO_3 .

Determination of molecular formula of a gaseous hydrocarbon by Eudiometric method :

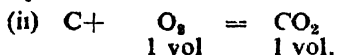
The molecular formula of a gaseous hydro-carbon is generally determined by exploding a known volume of it with excess of oxygen in a eudiometer and then noting down the volume of carbon dioxide formed and oxygen used up from the successive contractions in volume. In this method, the molecular formula is found out without knowing the percentage composition and molecular weight.

A known volume of pure hydrocarbon is mixed with a known volume of excess of pure oxygen in a eudiometer tube and exploded when the hydrocarbon is completely oxidised to carbon dioxide and steam. On cooling, a contraction in volume takes place which is due to condensation of steam to liquid water occupying a negligible volume and may also be due to volume changes produced as a result of the combustion.

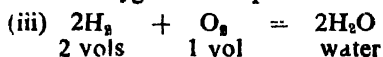
The residual gas mixture (carbon dioxide and oxygen) is then treated with NaOH or KOH which completely absorbs carbon dioxide. The second contraction in volume will give the volume of carbon dioxide formed. The residual gas whose volume is also noted is unused oxygen. All volumes are measured under the same conditions of temperature and pressure. Then, the formula of the

hydrocarbon can be arrived at from the volume of hydrocarbon taken, the first contraction in volume after sparking and the second on treatment with alkali.

In this connection, it should be noted that—(i) A part of the oxygen used produces carbon dioxide by oxidising the carbon present in the hydrocarbon and the other part converts hydrogen of the hydrocarbon to water.



∴ The volume of carbon dioxide produced is equal to the volume of oxygen used up in the oxidation of carbon.



In producing water, the volume of oxygen used up reacts with twice its own volume of hydrogen and this amount of hydrogen is available in the hydrocarbon.

For calculating the formula, three cases are to be considered.

(A) When the volume of oxygen added and two contractions are known.

(B) When the volume of oxygen added is not known but two contractions are known and the density of the hydrocarbon is not given.

(C) When the volume of oxygen added is not known but the density of the hydrocarbon and the first contraction are given.

Examples

[A] When the volume of oxygen added and two contractions are known :

(1) 20 ml of a gaseous hydrocarbon were mixed with 50 ml of oxygen and exploded in a eudiometer tube. On cooling, the volume was found to be 30 ml. On adding KOH, the volume was further reduced by 20 ml. Calculate the molecular formula of the hydrocarbon. (All volumes were measured under the same condition of temperature and pressure).

Vol. of hydrocarbon = 20 ml ; Vol. of oxygen taken = 50 ml

Second contraction -- Contraction in vol on treatment with KOH
-- vol. of CO_2 formed = 20 ml.

First contraction in vol = $20 + 50 - 30 = 40$ ml.

Vol of unused oxygen = $30 - 20 = 10$ ml.

Vol. of oxygen used up = $50 - 10 = 40$ ml.

Now, CO_2 contains its own volume of oxygen or 20 ml of CO_2 contain 20 ml of oxygen.

$\therefore (40 - 20) = 20$ ml oxygen have combined with hydrogen of the hydrocarbon to produce water. And 20 ml of oxygen must have combined with 40 c.c. of hydrogen. Hence,

20 ml of hydrocarbon contain 40 ml of hydrogen and give on explosion 20 ml of CO_2 .

Or, 1 vol. of hydrocarbon contains 2 vols of hydrogen and give 1 vol. of CO_2 on explosion.

Now, according to Avogadro's hypothesis 1 molecule of the hydrocarbon contains 2 molecules of hydrogen and gives 1 molecule of CO_2 .

So, 1 molecule of the hydrocarbon contains 4 atoms of hydrogen and 1 atom of carbon (\because Hydrogen molecule is diatomic and 1 molecule of CO_2 contains 1 atom of carbon).

Hence, the molecular formula of the hydrocarbon is CH_4 .

Alternative method: Let the formula of the hydrocarbon be C_xH_y . The balanced equation for its oxidation is



$$1 \text{ mol } (x + y/4) \text{ mol } x \text{ mol}$$

$$1 \text{ vol } (x + y/4) \text{ vol } x \text{ vol}$$

$$20 \text{ c.c. } 20(x + \frac{y}{4}) \text{ c.c. } 20x \text{ c.c.}$$

Vol of hydrocarbon taken = 20 c.c.

Vol of oxygen taken = 50 c.c.

Contraction with KOH = vol of CO_2 formed = 20 c.c.

Vol. of oxygen left unused = $50 - 20 = 30$ c.c.

Vol. of oxygen used up = $50 - 10 = 40$ c.c.

As shown by the equation given above, 20 c.c. of hydrocarbon requires $20(x + \frac{y}{4})$ c.c. of oxygen for combustion and will produce $20x$ c.c. of carbon dioxide.

$$20x = 20 \quad \text{or} \quad x = 1$$

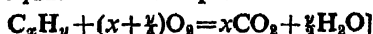
$$\text{also, } 20(x + \frac{y}{4}) = 40 \quad \text{or} \quad 20(1 + \frac{y}{4}) = 40 \quad \text{or} \quad y = 4$$

\therefore Mol. formula of the hydrocarbon = CH_4

[N.B. The equation for oxidation as given above can be derived thus—

When exploded with excess of oxygen, every molecule of the hydrocarbon of the formula C_xH_y will form x molecules of CO_2 and $\frac{y}{2}$ molecules of water. So, the total number of oxygen atoms required for the complete combustion of 1 molecule of hydrocarbon = $(2x + \frac{y}{2})$. or, the total number of oxygen molecules required for the purpose of combustion of 1 molecule of hydrocarbon = $x + \frac{y}{4}$

\therefore The equation for complete oxidation is



(2) 10 ml. of a gaseous hydrocarbon are exploded with 100 ml. of oxygen. The residual gas on cooling is found to measure 95 ml. of which 20 ml are absorbed by caustic potash and the rest by alkaline pyrogallol. Determine the formula of the hydrocarbon.

Vol of the gas absorbed by KOH = vol of CO_2 formed = 20 ml.

" " " " " " alk. pyrogallol = vol of unused oxygen = $95 - 20 = 75$ ml.

\therefore Vol. of oxygen used up $100 - 75 = 25$ ml.

Now, CO_2 contains its own volume of oxygen or 20 ml. of CO_2 formed contain 20 ml. of oxygen.

$\therefore (25 - 20) = 5$ ml. of oxygen have combined with hydrogen of the hydrocarbon to form water and 5 ml. of oxygen must have combined with the double vol. or 10 ml. of hydrogen.

\therefore 10 ml of the hydrocarbon contain 10 ml. of hydrogen and give 20 ml. of CO_2 .

Hence, according to Avogadro's hypothesis, 1 molecule of the hydrocarbon contains 1 molecule of hydrogen and gives 2 molecules of CO_2 . 2 molecules of CO_2 contain 2 atoms of carbon and 1 molecule of hydrogen contains 2 atoms of hydrogen. So 1 molecule of the hydrocarbon contains 2 atoms of carbon and 2 atoms of hydrogen.

\therefore The molecular formula of the hydrocarbon is C_2H_2 .

[B] When the volume of oxygen admitted is not known.

(3) 15 c.c. of a gaseous hydrocarbon were exploded with excess of oxygen and cooled. There was a contraction of 45 c.c. On treating with KOH, there was a further contraction of 45 c.c. Find the molecular formula of the hydrocarbon.

First contraction after explosion = 45 c.c.

Second contraction on treatment with KOH = vol of CO_2 formed = 45 c.c.

\therefore First contraction = vol. of hydrocarbon + vol. of oxygen used up - vol. of CO_2 formed

$\therefore 45 = 15 + \text{vol. of oxygen used up} - 45$

\therefore Vol. of O_2 used up = 75 c.c. = vol. of oxygen which has produced water and 45 c.c. of CO_2 from the hydrocarbon

45 c.c. of CO_2 contain 45 c.c. of oxygen

$\therefore (75 - 45)$ or 30 c.c. of oxygen have combined with hydrogen present in 15 c.c. of the hydrocarbon to produce water. Further this 30 c.c. of oxygen must have combined with 60 c.c. of hydrogen. Hence, 15 c.c. hydrocarbon contain 60 c.c. of hydrogen and give on combustion 45 c.c. of CO_2 . By Avogadro's hypothesis,

1 molecule of hydrocarbon contains 4 molecules or 8 atoms of hydrogen and gives 3 molecules of CO_2 .

Moreover, 3 molecules of CO_2 contain 3 atoms of carbon. Thus, the molecular formula of the hydrocarbon is C_3H_8 .

[C] When the volume of oxygen added is not known, only the 1st contraction and density of the hydrocarbon are known.

(4) 20 ml of a gaseous hydrocarbon are exploded with oxygen avoiding excess. On cooling, the volume contracts by 40 ml. The density of the hydrocarbon is 22. Find the formula of the hydrocarbon.

Let the molecular formula of the hydrocarbon be C_xH_y

Here, the contraction occurs as the vol. of the hydrocarbon and the vol. of oxygen used up for oxidation of carbon and hydrogen of the hydrocarbon are eliminated. Now the vol. of CO_2 formed is equal to the vol. of oxygen required to combine with carbon of the hydrocarbon.

The contraction = vol of the hydrocarbon + vol. of oxygen combined with carbon of the hydrocarbon + vol. of oxygen combined with the hydrogen of the hydrocarbon - vol. of CO_2 formed.

60 ml = 20 ml + vol of oxygen combined with hydrogen.

\therefore Vol. of oxygen combined with hydrogen = 60 - 20 = 40 ml.

The vol. of hydrogen present in the hydrocarbon is twice this vol. or $40 \times 2 = 80$ ml.

\therefore 20 ml. of the hydrocarbon contain 80 ml. of hydrogen

\therefore According to Avogadro's hypothesis.

1 molecule of the hydrocarbon contains 4 molecules or 8 atoms of hydrogen.

So, the hydrocarbon may be represented as C_xH_y

Molecular weight of the hydrocarbon = $12x + 8$

Density of the hydrocarbon = 22 (given)

\therefore Mol. wt of the hydrocarbon = $2 \times 22 = 44$

$\therefore 12x + 8 = 44 \quad \therefore x = 3$ (number of carbon atoms)

\therefore Molecular formula of the hydrocarbon is C_3H_8

Vapour density: The term vapour density has already been referred to in connection with one of the main deductions of Avogadro's hypothesis and it has been shown that the molecular weight of any gas is twice its vapour density.

The density of a substance means its mass per unit volume. The density obtained by expressing the mass in grams and the volume it occupies in millilitres is called the absolute density.

$$\therefore \text{density } (d) = \frac{m \text{ (mass of the substance)}}{v \text{ (volume of the substance)}}$$

$$\therefore d = \frac{m}{v} \quad \text{gms} = \frac{\text{Wt. of the substance (in gms)}}{\text{Vol. of the substance (in ml)}} \\ = \text{Absolute density.}$$

It is to be noted that the density has a unit. The volume of a gas has a marked sensitivity to changes of temperature and pressure although its mass remains unaltered. It is obvious that the density of a gas changes considerably even for minor changes of temperature or pressure. Hence when the density of a gas is stated, its temperature and pressure must be mentioned.

For a gas, the absolute density is very low. So, the density of a gas is generally expressed as the normal density which is the weight of 1 litre of the gas at N.T.P. At N.T.P. the density of hydrogen is 0.000089 gm and that of carbon dioxide is 0.00198. Therefore, the normal densities of hydrogen and carbon dioxide are 0.089 or 0.09 (approx.) gm and 1.98 gms. respectively.

For various reasons, the vapour density or relative density is preferably used in place of normal density.

The vapour density is a number that represents how many times the given volume of a gas is heavier than the same volume of hydrogen under the same conditions of temperature and pressure.

$$\therefore \text{Vapour density} = \frac{\text{wt. of a given vol. of a gas or vapour}}{\text{wt. of an equal vol. of hydrogen}}$$

As the vapour density is a pure number it has no unit.

$$\text{Vapour density of CO}_2 = \frac{\text{wt. of V c.c. of carbon dioxide}}{\text{wt. of V c.c. of hydrogen}} \\ \text{(Under the similar conditions of temp. and pressure)} \\ = \frac{\text{wt. of 1 c.c. of carbon dioxide}}{\text{wt. of 1 c.c. of hydrogen}} \\ \text{(under similar condition)}$$

$$= \frac{0.00198}{0.00009} = 22.$$

\therefore Vapour density of carbon dioxide is 22 ($H=1$)

The density of a gas changes with the temperature but its relative density is independent of the temperature.

The normal density of hydrogen = 0.09 gm

Relative density or vapour density of a gas

$$= \frac{\text{normal density of the gas}}{\text{normal density of hydrogen}}$$

\therefore normal density of a gas = vapour density \times 0.09

i.e. wt. of 1 litre of any gas at N.T.P. = vapour density \times 0.09

The relative density of vapour produced on vaporisation of a solid or a liquid substance is also expressed as the ratio of the density of vapour to that of hydrogen. Thus, the vapour densities of water vapour and chloroform are 9 and 59.68 respectively.

Empirical and Molecular formulas :

Empirical formula : The empirical formula of a compound is the simplest formula which expresses the simple whole number ratio of atoms of its constituent elements or the relative number of each kind of atom present in the molecule and is deduced from the percentage composition of the compound.

Molecular formula : The molecular formula of a compound represents the actual number of atoms of each of the constituent elements present in one molecule of it.

Thus, the empirical formula denotes merely the atomic ratios but the molecular formula gives the exact number of atoms of various elements constituting the molecule of a compound.

For example,

Benzene is a compound of carbon and hydrogen. Analysis shows that the ratio of atom of carbon to that of hydrogen in the compound is 1 : 1 i.e. its empirical formula is CH. But actually, a molecule of benzene consists of 6 atoms of carbon and 6 atoms of hydrogen. So, the molecular formula of benzene is C_6H_6 . Similarly, the empirical formula of hydrogen peroxide is HO while its molecular formula is H_2O_2 .

Calculation of Empirical and Molecular formulae—Relation between the two :

Calculation of empirical formula : Let two elements A and B combine chemically to form a compound having the formula A_xB_y , where x and y are the number of atoms of A and B respectively. Let a and b stand for the atomic weights of A and B respectively.

\therefore Molecular weight of the compound $A_xB_y = ax + by$

\therefore The percentage of A = $\frac{ax \times 100}{ax + by}$ and

the percentage of B = $\frac{by \times 100}{ax + by}$

$\therefore \frac{\text{percentage of A}}{\text{percentage of B}} = \frac{ax \times 100}{ax + by} \times \frac{ax + by}{by \times 100} = \frac{ax}{by}$

$\therefore \frac{\text{percentage of A}}{a} : \frac{\text{percentage of B}}{b} = x : y$

Or, $\frac{\text{percentage of A}}{\text{atomic weight of A}} : \frac{\text{percentage of B}}{\text{atomic weight of B}}$

= number of atoms of A : number of atoms of B. From the above, it is evident that the number obtained by dividing the percentage of an element by its atomic weight is directly proportional to the number of atoms of that element in the molecule of the compound. Hence, the relative number of each kind of atom can be found out from the percentage composition of the

compound. On this basis, calculation of empirical formula involves the following steps.

(i) The percentage of each element is divided by its atomic weight so as to get the ratio of the number of atoms present.

(ii) If the ratio contains fractional terms, it is to be expressed in whole numbers by dividing each term by the lowest one. (H.C.F.)

This is necessary because atoms are indivisible and number of atoms in a formula must be integral.

(iii) If the figures thus obtained are still not whole numbers, they are further reduced to whole numbers by multiplying with the smallest whole number. Sometimes, minor fractions are neglected and rule of approximation is applied for getting the whole number.

The simple atomic ratio so obtained gives the empirical formula of the compound.

Calculation of molecular formula : The molecular formula of a compound may be the same as the empirical formula or a simple multiple of it. The two formulae are related to each other as

$$\text{Molecular formula} = (\text{Empirical formula})_n$$

where n is a simple integer and may have values 1, 2, 3, 4 and so on. Thus when $n=1$, there is no difference between the molecular formula and the empirical formula. It follows from the above relation that

$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

∴ The value of n is easily obtained by dividing the molecular weight of the compound by its empirical formula weight.

The empirical formula weight is the sum of atomic weights of all the atoms of different elements present in the formula

So, the empirical formula when multiplied by the value of n gives the molecular formula. As has been shown above, the determination of the value of n requires the knowledge of molecular weight of the compound.

Illustrations : Water is a binary compound of hydrogen and oxygen. The ratio between the atoms of hydrogen and oxygen in the compound has been calculated as 2 : 1 i.e. its empirical formula is H_2O . So its molecular formula is $(\text{H}_2\text{O})_n$. From the molecular weight, the value of n is found to be 1. Evidently in the case of water, its molecular formula coincides with the empirical formula.

Ethylene is a hydrocarbon. In the compound, number of atoms of carbon : no. of atoms of hydrogen = 1 : 2 i.e. its empirical formula is CH_2 .

∴ Its molecular formula is $(\text{CH}_2)_n$. From the knowledge of

molecular weight of ethylene, n has been found to be equal to 2. So the molecular formula of ethylene is C_2H_4 .

Numerical problems on empirical and molecular formulae :

(1) A colourless crystalline compound has the following percentage composition; Sulphur 24.24%, nitrogen 21.21%, hydrogen 6.06%; the rest is oxygen. Determine the empirical formula of the compound. Give the name of the compound if the molecular formula be the same as the empirical formula and if it is found to be a sulphate.

% of oxygen by difference = $100 - (24.24 + 21.21 + 6.06) = 48.49$
Dividing the percentage composition by the at. wts. we have,

$$\begin{aligned}\text{Ratio of atoms, S : N : H : O} &= \frac{24.24}{32} : \frac{21.21}{14} : \frac{6.06}{1} : \frac{48.49}{16} \\ &= 0.757 : 1.515 : 6.06 : 3.03 \\ &= 1 : 2 : 8 : 4 \quad (\text{Dividing each by} \\ &\quad \text{the lowest number } 0.757)\end{aligned}$$

\therefore The empirical formula of the compound is $SN_2H_8O_4$. As the empirical formula and molecular formula of the compound are same and the compound is a sulphate, the compound is $N_2H_8(SO_4)_2$ or $(NH_4)_2SO_4$.

\therefore The name of the compound is ammonium sulphate.

(2) The atomic weight of an element is found to be 24. The oxide of the element contains 40% of oxygen. Find the empirical formula of the oxide.

Let the element be represented by M .

The oxide contains 40% of oxygen,

So it contains $(100 - 40)$ or 60% of M .

$$\text{Ratio of atoms, M : O} = \frac{60}{24} : \frac{40}{16} = 2.5 : 2.5 = 1 : 1$$

The empirical formula of the oxide is MO .

(3) An iron oxide mineral on analysis is found to contain 42% iron. The mineral also contains 42% impurity. Find the empirical formula of the oxide present in the mineral. (Fe = 56)

% of impurity present in the mineral = 42

\therefore The mineral contains $(100 - 42) = 58\%$ of oxide.

So, the iron oxide contains $(58 - 42) = 16\%$ of oxygen.

\therefore Ratio of weights Fe : O = 42 : 16

$$\text{and } \therefore \text{ atoms, Fe : O} = \frac{42}{56} : \frac{16}{16} = \frac{3}{4} : 1 \text{ or } 3 : 4$$

\therefore The empirical formula of the oxide is Fe_3O_4

(4) A compound of carbon, hydrogen and chlorine contains C=10.04%, H=0.84%, Cl=89.12%. Its vapour density was found to be 59.75. What is the molecular formula of the compound?

Ratio of % weights, C : H : Cl = 10.04 : 0.84 : 89.12

Dividing the percentage composition by the at. wts, we have

$$\begin{aligned}\text{ratio of atoms, C : H : Cl} &= \frac{10.04}{12} : \frac{0.84}{1} : \frac{89.12}{35.5} \\ &= 0.84 : 0.84 : 2.51 \\ &= 1 : 1 : 3 \text{ (dividing each by} \\ &\quad \text{the lowest number 0.84).}\end{aligned}$$

∴ The empirical formula of the compound is CHCl_3 and the molecular formula is $(\text{CHCl}_3)_n$ where n is a whole number.

As per data given, the vapour density of the compound is 59.75.

∴ Molecular weight of the compound = $2 \times 59.75 = 119.50$ i.e. $(\text{CHCl}_3)_n = 119.50$.

$$\text{So, } n = \frac{\text{Mol. wt.}}{\text{Empirical formula wt.}} = \frac{119.50}{12 + 1 + 35.5 \times 3} = 1$$

∴ Molecular formula = CHCl_3 .

(5) A compound of carbon, hydrogen and oxygen contains C=40%, H=6.67%. When the compound is vaporised, its vapour density is found to be 2.813 times than that of oxygen. Find the empirical and molecular formulae of the compound.

% of oxygen by difference = $100 - (40 + 6.67) = 53.33$

So ratio of weights C : H : O = 40 : 6.67 : 53.33

$$\begin{aligned}\text{and, , , atoms C : H : O} &= \frac{40}{12} : \frac{6.67}{1} : \frac{53.33}{16} \\ &= 3.33 : 6.67 : 3.33 = 1 : 2 : 1 \text{ (dividing} \\ &\quad \text{by 3.33)}\end{aligned}$$

∴ Empirical formula = CH_2O

Vapour density of the gas = $2.813 \times 16 = 45$

∴ Molecular weight = $2 \times 45 = 90$

Let the molecular formula = $(\text{CH}_2\text{O})_n$ [n = a whole number]

∴ $(\text{CH}_2\text{O})_n = 90$; ∴ $n(12 + 2 + 16) = 90$ or $n = 3$

Hence the molecular formula is $\text{C}_3\text{H}_6\text{O}_3$.

(6) A compound contains 41.38% carbon, 3.45% hydrogen and the rest oxygen. Its molecular weight is 116. Calculate its molecular formula.

0.25 gm. of the compound was burnt completely in carbon-dioxide-free dry air. The gaseous products formed were passed through two U-tubes containing fused calcium chloride and caustic soda respectively. Find out the gain in weights of the two tubes.

$$C=41.38\%, H=3.45\% \therefore O=100-(41.38+3.45)=55.17\%$$

$$\text{So the ratio of weights } C : H : O = 41.38 : 3.45 : 55.17$$

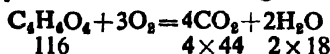
$$\begin{aligned} \text{and the ratio of atoms } C : H : O &= \frac{41.38}{12} : \frac{3.45}{1} : \frac{55.17}{16} \\ &= 3.45 : 3.45 : 3.45 \\ &= 1 : 1 : 1 \end{aligned}$$

\therefore Empirical formula of the compound = CHO and the molecular formula = $(CHO)_n$ where $n = a$ whole number

$$n = \frac{\text{mol. wt}}{\text{Emp. formula wt.}} = \frac{116}{12+1+16} = 4$$

Hence, the molecular formula $C_4H_4O_4$

The compound on combustion gives carbon dioxide and water.



When burnt in air,

116 gms. of the compound give 176 gms. of carbon dioxide

$$\therefore 0.25 \text{ gm. } ,, ,, \text{ gives } \frac{176 \times 0.25}{116} \text{ or } 0.3793 \text{ gm. of carbon dioxide}$$

Again, 116 gms of the compound produce 36 gms of water

$$\therefore 0.25 \text{ gm. } ,, ,, \text{ produces } \frac{36 \times 0.25}{116} \text{ or } 0.0776 \text{ gm. of water.}$$

Now, weights of both the tubes will be increased as the fused calcium chloride absorbs water and carbon dioxide is absorbed by caustic soda. So the gain in wt. of the tube containing fused calcium chloride is 0.0776 gm. and that of the tube containing caustic soda is 0.3793 gm.

(7) A metal M forms two oxides containing 27.6 and 30 percent of oxygen respectively. The formula of the first oxide is M_2O_4 . Find the atomic weight of M and the formula of the second oxide.

$$\text{In the first oxide, } O=27.6\% \therefore \text{The metal } M = 100 - 27.6 = 72.4\%$$

$$\text{In the second oxide, } O=30\% \therefore M = 100 - 30 = 70\%$$

Let the atomic weight of M be a . So in the first oxide,

$$M : O = \frac{72.4}{a} : \frac{27.6}{16} = 3 : 4$$

$$\text{i.e. } \frac{72.4 \times 16}{a \times 27.6} = \frac{3}{4} \text{ or } a = \frac{72.4 \times 16 \times 4}{27.6 \times 3} = 56 \text{ (approx.)}$$

$$\therefore \text{ in the second oxide, } M : O = \frac{70}{56} : \frac{30}{16} \text{ or } 2 : 3$$

\therefore The formula of the second oxide is M_2O_3 .

CHAPTER 5

EQUIVALENT WEIGHT

It follows from the law of reciprocal proportion that every element must have a definite weight in which or in integral multiples of which, it combines with other elements and consequently the proportions by weight in which the chemical combination between two elements takes place are known from the same law. In support of these, the results of analysis of some hydrogen-compounds are shown below.

Compounds and formulae	Analytical results
Methane, CH_4 1 part by wt. of hydrogen combines with 3 parts by wt. of carbon	
Water, H_2O 1 " " " " " " " " 8 parts by wt. of oxygen	
Hydrogen sulphide, H_2S 1 part by " " " " " " " " 16 parts by wt. of sulphur	
Hydrogen chloride, HCl 1 " " " " " " " " 35.5 parts by wt. of chlorine	
Hydrogen bromide, HBr 1 " " " " " " " " 80 parts by wt. of bromine	
Sodium hydride, NaH 1 " " " " " " " " 23 parts by wt. of sodium	
Calcium hydride CaH_2 1 " " " " " " " " 20 parts by wt. of calcium	
Ammonia, NH_3 1 " " " " " " " " 4.67 parts by wt. of nitrogen	

It is seen from the above analytical results that a definite quantity of each of the elements on the right hand side unites chemically with a definite weight of hydrogen (i.e. 1 part by wt. of hydrogen). It is further observed that these elements shall combine (if they combine at all) with each other in proportions of the weights shown or in simple multiples of them.

This will be clearly understood if we note the ratio of the combining weights of the constituent elements in their binary compounds.

Compound	Ratio of wts. of constituent elements
Carbon dioxide (CO_2)	wt. of carbon : wt. of oxygen = 3 : 8
Carbon tetrachloride (CCl_4)	wt. of carbon : wt. of chlorine = 3 : 35.5
Sodium chloride (NaCl)	wt. of sodium : wt. of chlorine = 23 : 35.5
Calcium sulphide (CaS)	wt. of calcium : wt. of sulphur = 40 : 16

It is evident from these examples that the weights in which the elements carbon, oxygen, chlorine, sodium, calcium sulphur separately combine with a fixed weight of hydrogen (1 part) are also the weights in which two of the elements combine with each other.

Similarly, results of careful analysis of suitable compounds will reveal that all elements are associated with definite numbers expressing the parts by weights in which they combine with one another. These numbers representing weights are called the equivalent weights or combining weights or chemical equivalents or simply equivalents of the elements. The idea of equivalent weights has been expressed in the fig. 1 (18).

The concept of equivalent weight is not only applicable in chemical combinations but also in the displacement of one element from a compound by another. Thus, it follows from the above discussions that the elements always combine with or displace each other in the ratio of their equivalents.

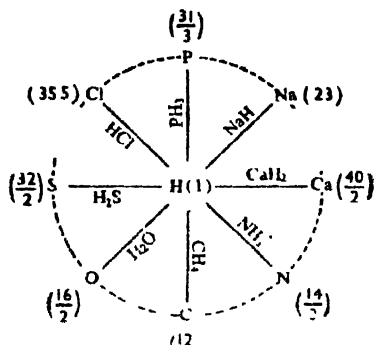


Fig. 1(18)
Equivalent weights

The equivalent weight is a quantity to be determined experimentally. So for its numerical expression, it is necessary to have a standard of reference. Originally, 1 part by weight of hydrogen was chosen as the standard by Dalton. (We have so far discussed equivalent weights in terms of hydrogen). But since many elements, particularly metals, are incapable of forming stable compounds with hydrogen, the standard of equivalent weights was changed to oxygen. At present 8 parts by weight of oxygen has been accepted as the standard of reference. On the basis of the oxygen scale, the equivalent weight of hydrogen is 1.008 and that of chlorine is 35.46. Similarly, minor changes in the values of equivalent weight of other elements will be observed if calculated with reference to oxygen instead of hydrogen. As some elements form well-defined and easily purifiable chlorides 35.46 parts by weight of chlorine is sometimes taken as the standard. Practically, now a days, equivalent weight is expressed in terms of 8 parts by weight of oxygen or its equivalent e.g. 1.008 parts by weight of hydrogen or 35.46 parts by weight of chlorine.

When an element forms more than one compound with another element (say oxygen), the equivalent weights will differ in these cases but the values will bear a simple integral ratio to one another. For example,

The elements carbon (eq. wt. 3) and oxygen (eq. wt. 8) will combine to form two different compounds.

In carbon dioxide (CO_2), wt of oxygen : wt of carbon = 8 : 3.002

In carbon monoxide (CO), wt of oxygen : wt of carbon
= 8 : 6.004

Again, sodium (eq. wt 22.99) will combine chemically with oxygen to produce two oxides.

In sodium monoxide (Na_2O), wt of oxygen : wt of sodium =
8 : 22.99

In sodium peroxide (Na_2O_2), wt. of oxygen : wt. of sodium
= 8 : 11.495

Thus, the elements combine with one another in the ratio of either their equivalent weights or simple multiples of them. This is the *law of equivalent proportions* and may be taken as another form of the law of reciprocal proportions. It will be seen later that an element with a variable valency will have more than one equivalent weight. ✓

Equivalent weight or Chemical equivalent :

Definition : The equivalent weight or chemical equivalent of an element is the number of parts of it which can combine chemically with or can displace from a compound directly or indirectly, 8.000 parts by weight of oxygen (or 1.008 parts by weight of hydrogen or 35.46 parts by weight of chlorine).

It is to be borne in mind that the chemical equivalent of a given element is a ratio of the weight of the element to a definite weight of a standard element. So it is a pure number and does not have any unit.

Thus,

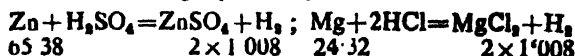
$$\text{Eq. wt.} = \frac{\text{wt. of the element} \times 1.008}{\text{wt. of hydrogen combined or displaced}}$$

$$\text{or, } \frac{\text{wt. of the element} \times 8}{\text{wt. of oxygen combined or displaced}}$$

$$\text{or, } \frac{\text{wt. of the element} \times 35.46}{\text{wt. of chlorine combined or displaced}}$$

Illustrations : (a) On analysis of the compounds sodium hydride (NaH), hydrogen bromide (HBr) and hydrogen sulphide (H_2S), we find that 1.008 parts by weight of hydrogen unite separately with 22.99 parts by weight of sodium, 79.916 parts by weight of bromine and 16 parts by weight of sulphur. So, the equivalent weights of sodium, bromine and sulphur are 22.99, 79.916 and 16 respectively.

(b) In the following equations,



We find that 65.38 parts by weight of zinc displace 2.016 parts by weight of hydrogen from the acid or 32.69 parts by weight of zinc displace 1.008 parts by weight of hydrogen. Similarly 12.16 parts by weight of magnesium displace 1.008 parts by weight of hydrogen. Therefore, the equivalent weights of zinc and magnesium are 32.69 and 12.16 respectively.

(c) In calcium oxide (CaO), 16 parts by weight of oxygen combine with 40.08 parts by weight of calcium or 8 parts by weight of oxygen are in combination with 20.04 parts by weight of calcium. \therefore 20.04 is the equivalent weight of calcium. In carbon dioxide (CO_2), 32 parts by weight of oxygen combine with 12 parts by weight of carbon or 8 parts by weight of oxygen combine with 3 parts by weight of carbon. Hence equivalent weight of carbon is 3.

(d) In aluminium chloride (AlCl_3), 3×35.46 parts by weight of chlorine combine with 26.96 parts by weight of aluminium. So the equivalent weight of aluminium—8.99.

Equivalent weight of a radical: We know that a radical behaves like an element. \therefore , the equivalent weight of a radical represents how many parts by weight of it can combine with 1.008 parts by weight of hydrogen or the equivalent of any other element or a radical.

It is seen that in nitric acid (HNO_3), $(14.008 + 48)$ or 62.008 parts by weight of nitrate radical (NO_3) are in combination with 1.008 parts by weight of hydrogen. \therefore Equivalent weight of $\text{NO}_3 = 62.008$. In sodium carbonate (Na_2CO_3), 2×22.99 parts by weight of sodium combine with $(12.01 + 48)$ or 60.01 parts by weight of the carbonate radical (CO_3). Or, 22.99 parts by weight of sodium (equivalent weight of sodium) are in combination with 30.005 parts by weight of the carbonate radical. \therefore Equivalent weight of $\text{CO}_3 = 30.005$. In ammonium nitrate (NH_4NO_3), 62.008 parts by weight of the nitrate radical (1 equivalent of NO_3) are found to combine with 18.04 parts by weight of ammonium radical (NH_4). Hence, the equivalent weight of $\text{NH}_4 = 18.04$.

Equivalent weight of a compound: The concept of equivalent weight has been extended also to the compounds.

The equivalent weight of a compound is the number of parts by weight of the compound which is obtained by adding the equivalent weights of its constituent elements or radicals. Thus—

Compound	Eq. wts of constituents	Eq. wt. of comp.
H_2SO_4	H—1.008 ; SO_4 —48	49.008
AgNO_3	Ag—107.88 ; NO_3 —62.008	169.888
AlCl_3	Al—8.99 ; Cl—35.46	44.45

Alternately, the equivalent weight of a compound represents how many parts by weight of it contain or react with 8.000 parts by

weight of active oxygen or 1.008 parts by weight of hydrogen or an equivalent of any substance.

Detailed discussions on eq. wts of some compounds will be given in the next chapter.

Gram-equivalent : The equivalent weight expressed in grams is known as the gram-equivalent. The gram-equivalents of oxygen, sodium, silver nitrate, sulphuric acid are 8 gms of oxygen, 22.99 grams of sodium, 169.888 gms of silver nitrate and 49.008 gms of sulphuric acid respectively.

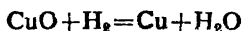
A more elaborate definition of gram-equivalent is also given below :

The gram-equivalent of a substance is that weight of it (in gms) which will combine with, displace or contains 1.008 gms of hydrogen (i.e. 11.2 litres of hydrogen measured at N. T. P.) or 8 gms of oxygen (i.e. 5.6 litres of oxygen at N. T. P.) or 35.46 gms of chlorine (i.e. 11.2 litres of chlorine at N. T. P.) or the known equivalent of any other substance.

Determination of equivalent weights of elements : Different methods employed in determining the equivalent weights of both non-metallic and metallic elements are described below :

✓(1) **Equivalent weights of non-metals :** (A) **Determination of equivalent weight of oxygen—Duma's method :** (by direct union with hydrogen or reduction of a metallic oxide).

Principle : A current of pure and dry hydrogen is passed through a weighed quantity of cupric oxide when hydrogen reduces the oxide to metallic copper and itself combines with the oxygen of cupric oxide to form water.



The weights of hydrogen and oxygen involved in the combination are determined from the weight of water produced and the loss in weight of cupric oxide. The parts by weight of oxygen combining with 1.008 parts by weight of hydrogen will represent the equivalent weight of oxygen.

Experimental procedure : A small quantity of pure and dry black cupric oxide is taken in a hard glass combustion tube having a bulb in the middle. The bulb tube with its content (CuO) is accurately weighed. One end of the bulb tube is connected with a previously weighed U-tube containing fused calcium chloride. To prevent the entry of water vapour into the U-tube from outside, a guard tube filled with fused calcium chloride is attached with the open end of the U tube (not shown in the fig.). Then a stream of pure and dry hydrogen is passed through the other end of the combustion tube. When the air from inside the whole apparatus is removed, the tube is strongly heated. At the high temperature,

hydrogen and cupric oxide interact to produce metallic copper and steam. The steam is driven away by hydrogen and is absorbed in the calcium chloride U-tube. When all the black cupric oxide is completely converted into red copper, heating is stopped and the whole apparatus is allowed to cool down to the room temperature

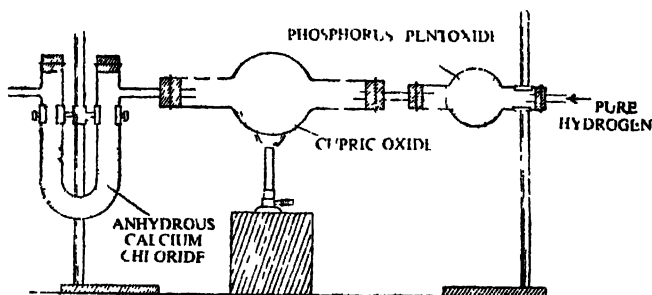


Fig. 1(19) Determination of equivalent weight of oxygen

in the current of hydrogen. After cooling, the bulb tube and the calcium chloride U-tube are detached and separately weighed. The weight of oxygen that has combined with hydrogen to produce water is known from the loss in the weight of the combustion tube while the increase in the weight of calcium chloride U-tube gives the weight of water formed.

Calculations : Let

wt. of combustion tube + cupric oxide before expt. = W gms.

“ “ “ “ + Cu after “ = W_1 “

∴ wt. of oxygen = $(W - W_1)$ gms.

wt. of CaCl_2 U-tube before expt. = W_2 gms.

“ “ “ “ after “ = W_3 gms.

∴ wt. of water produced = $(W_3 - W_2)$ gms.

wt. of hydrogen taken part in combination

= $(W_3 - W_2) - (W - W_1)$ gms. = x gms. (say)

∴ x gms of hydrogen combine with $(W - W_1)$ gms of oxygen

∴ 1.008 gms “ “ “ “ $\frac{(W - W_1) \times 1.008}{x}$

gms of oxygen

So, equivalent wt. of oxygen = $\frac{(W - W_1) \times 1.008}{(W_3 - W_2) - (W - W_1)}$

✓(B) Determination of equivalent weight of carbon : (By direct combination with oxygen).

Principle : A weighed quantity of pure carbon is converted into carbon dioxide by heating it in a stream of pure and dry oxygen. Carbon dioxide produced is absorbed in strong caustic

potash solution and its weight is taken. The weight of oxygen that has combined with the known weight of carbon can be obtained from the weight of carbon dioxide produced. Thus, the equivalent weight is determined from the relation.

$$\text{Equivalent wt. of carbon} = \frac{\text{Wt. of carbon taken} \times 8}{\text{Wt. of oxygen combined}}$$

Experimental procedure: The exact weight of a clean and perfectly dry porcelain boat is taken. A small quantity (about 1 gm) of pure charcoal (sugar charcoal) is placed into it and weighed again. The boat with charcoal is then introduced into a hard-glass tube nearly one half of which is packed with dry cupric oxide from an open end. The end of the tube nearer the boat is connected with an apparatus supplying pure and dry oxygen. A slow stream of the gas is passed for some time through the tube so as to displace the air from inside by oxygen and the other end is attached to previously weighed potash bulbs containing strong caustic potash solution. A calcium chloride guard-tube together with a U-tube filled with soda lime is also attached to the free end of the potash bulbs to prevent the entry of atmospheric carbon dioxide or water vapour into the bulbs.

The hard glass tube is then laid in a furnace in such a way that both of its ends remain outside the furnace. The layer of cupric oxide and the boat containing carbon are then strongly heated while a slow stream of oxygen is continually passed through the combustion tube. The charcoal at the high temperature is oxidised by

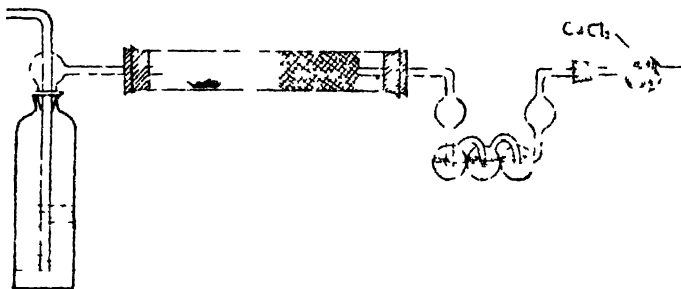
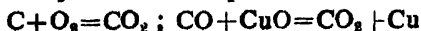


Fig. 1(20) Determination of equivalent weight of carbon

oxygen to carbon dioxide; any carbon monoxide which may simultaneously be formed due to shortage of oxygen is converted into carbon dioxide by the heated cupric oxide.



The carbon dioxide thus formed is swept away by the oxygen gas and is absorbed in the potash bulbs.

When the charcoal is completely burnt away, heating is stopped; but oxygen is passed through the tube for some time to ensure that

all the carbon dioxide formed has been driven away and absorbed. When cooled to room temperature, the potash bulbs are re-weighed carefully.

Calculation : Let

wt. of the empty boat = W gms.

wt. of boat + charcoal before expt = W_1 gms.

\therefore wt of carbon taken = $(W_1 - W)$ gms.

wt. of the potash bulbs before expt. = W_2 gms.

“ “ “ “ “ after “ = W_3 gms.

\therefore Wt. of carbon dioxide produced = $(W_3 - W_2)$ gms.

and wt. of oxygen = wt. of carbon dioxide - wt. of carbon
 $= \{(W_3 - W_2) - (W_1 - W)\}$ gms.

$\therefore \{(W_3 - W_2) - (W_1 - W)\}$ gms. of oxygen combine with $(W_1 - W)$ gms. of carbon.

\therefore 8 gms. of oxygen combine with $\frac{(W_1 - W) \times 8}{(W_3 - W_2) - (W_1 - W)}$ gms. of carbon

\therefore Equivalent wt. of carbon = $\frac{(W_1 - W) \times 8}{(W_3 - W_2) - (W_1 - W)}$

This method is generally employed in cases of elements (like sulphur, phosphorus) which form volatile gaseous oxides.

(2) Determination of equivalent weights of metals

(a) Hydrogen-displacement method : The method is applicable to metals like zinc, iron, magnesium etc. which react with dilute mineral acids easily at room temperature with the evolution of hydrogen. A certain known weight of the metal is allowed to dissolve in excess of dilute acid and the weight of liberated hydrogen is found out from its volume. Then the equivalent weight of the given metal can be determined from the relation,

$$\text{Equivalent wt. of metal} = \frac{\text{Wt. of the metal} \times 1.008}{\text{Wt. of hydrogen displaced}}$$

It is to be remembered that the wt of hydrogen cannot be obtained directly. The wt. of hydrogen in gms. is calculated as follows.

Firstly, the volume of hydrogen displaced is measured in ml. and reduced to N. T. P. Secondly the vol at N. T. P. is multiplied by 0.00089 (the wt of 1 ml. of hydrogen at N.T.P. is 0.00089 gms. according to Avogadro's hypothesis)

So the wt. of H_2 in gm. = Vol. in ml of H_2 at N.T.P. $\times 0.00089$

✓ **Equivalent weight of zinc :**

Procedure : An accurately weighed quantity of zinc (about 0.08 gm.) is taken in a watch glass which is then placed at the

bottom of a beaker. Zinc in the watch glass is covered with an inverted funnel. Water is poured till the stem of the funnel remains completely immersed under water. A graduated tube closed at one end is filled completely with water and inverted carefully over the stem of the funnel so that the whole stem remains inside the tube. The tube is then clamped with a stand.

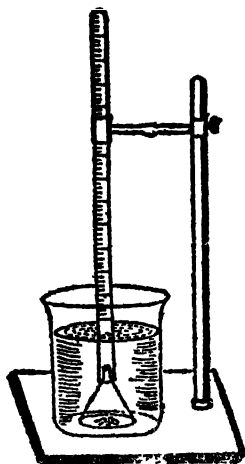


Fig. 1(21)

Determination of equivalent weight of zinc

The surface of water inside and outside the tube is then brought to the same level* by dipping or raising it in the water of the jar. During this operation, the tube is held with a piece of paper and not with the fingers.

Now the volume of hydrogen is noted carefully, so also the temperature of water and the atmospheric pressure.

Calculation : Let

Wt. of zinc used = w gms.

Vol. of hydrogen collected = V c.c.

Temp. of the room during expt = $t^{\circ}\text{C}$.

Atmospheric pressure = P m.m.

Tension of aqueous vapour at $t^{\circ}\text{C}$ = f m.m.

\therefore Actual pressure of dry hydrogen = $(P - f)$ m.m.

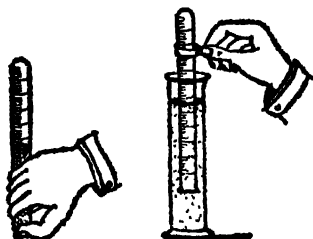


Fig. 1(22)

* Under this condition, the pressure of hydrogen gas becomes equal to the atmospheric pressure at the temperature of the laboratory.

(Since hydrogen is collected over water, it is moist and the atmospheric pressure = pressure of hydrogen + tension of water vapour at $t^{\circ}\text{C}$)

Let the volume of hydrogen ($V_{\text{ml.}}$) at $t^{\circ}\text{C}$ and $(P-f)$ pressure occupies V_0 ml. at N. T. P. Applying the Boyle's and Charles' laws, we get.

$$\frac{(P-f) \times V}{t+273} = \frac{V_0 \times 760}{273} \quad \text{or, } V_0 = \frac{(P-f) \times V \times 273}{(t+273) \times 760} \text{ ml.}$$

Wt. of 1 ml. of hydrogen at N. T. P. (according to Avogadro's hypothesis) = 0.000089 gm.

$$\therefore \text{wt. of } V_0 \text{ ml. of hydrogen} = V_0 \times 0.000089 \text{ gm.}$$

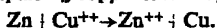
= Wt. of hydrogen displaced by w gms. of zinc.

$$\therefore \text{Equivalent wt. of zinc} = \frac{w \times 1.008}{V_0 \times 0.000089}$$

$$\text{or, } \frac{w \times 1.018 \times (t+273) \times 760}{(P-f) \times V \times 273 \times 0.000089}$$

N B (i) The above calculation requires the application of the gas equation derived from Boyle's and Charles' laws and also Dalton's law of partial pressure. These laws have been discussed in the chapter 8.

(ii) In the above expt. a few drops of copper sulphate solution are added as the pure zinc does not react with dil. acid appreciably. Since zinc occupies a higher position than copper in the electro-chemical series (vide chapter 7), a very small amount of zinc is lost in displacing copper from copper sulphate solution.



But this loss is however so small that it can be neglected. (iii) To determine the equivalent wt. of aluminium, dil. hydrochloric acid is used instead of dil. sulphuric acid. It is not necessary to add copper sulphate solution in this case. (iv) In this method, a small amount of the metal must be used so that the hydrogen evolved is conveniently collected in the graduated tube. The wt. of zinc taken in this expt. must not exceed 0.1 gm. and in case of magnesium, its wt. should be less than 0.05 gm. (iv) The gas measuring tube must be held with the help of a strip of paper and not with the fingers as the warmth of the hand will expand the vol. of the gas.

(B) Oxide-formation method : A weighed quantity of the metal is either directly or indirectly converted into its oxide. The weight of the combined oxygen can be found out from the weight of the oxide produced. The parts by weight of the metal combining with 8.000 parts by weight of oxygen will give the equivalent wt. of the metal.

Equivalent weight of magnesium (by direct formation of oxide) : The constant weight of a clean and dry porcelain crucible with its lid is taken. A piece of well cleaned magnesium ribbon is introduced in the crucible which is weighed again. The crucible with the metal and the lid is placed on a tripod-

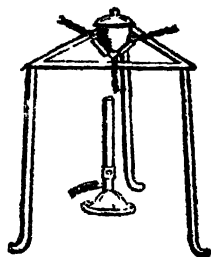
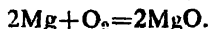


Fig. 1(23)

stand with the help of a clay-pipe triangle [fig. 1(23)] and is heated slowly. While heating, the lid is put slightly on one side so that air may come in contact with magnesium and magnesium oxide formed does not escape into the atmosphere. When the metal is burnt completely to its oxide, the crucible is cooled in a desiccator and weighed again. The process of heating, cooling and weighing is repeated till the two successive weights are found to be the same.



Calculation : Let

wt. of the empty crucible with lid = W gms.

wt. of the crucible with lid + magnesium = W_1 gms.

\therefore Wt. of magnesium taken = $(W_1 - W)$ gms.

Again,

Wt. of the crucible with lid + magnesium oxide = W_2 gms.

\therefore wt. of oxygen combined = $(W_2 - W_1)$ gms.

$\therefore (W_2 - W_1)$ gms. of oxygen combine with $(W_1 - W)$ gms. of magnesium

\therefore 8 " " " " " " $\frac{(W_1 - W) \times 8}{(W_2 - W_1)}$ gms. of magnesium

$$\therefore \text{Eq. wt. of magnesium} = \frac{(W_1 - W) \times 8}{(W_2 - W_1)}$$

In the above process, a portion of magnesium oxide may escape into the air during heating and the heated magnesium may form a little nitride (Mg_3N_2) in addition to its oxide (MgO). Thus, the method is not an accurate one and is not used in practice.

✓ **Equivalent weight of copper (by indirect formation of oxide) :**

Principle : A weighed quantity of copper is dissolved in concentrated nitric acid and the resulting solution is slowly evaporated to dryness. The solid nitrate thus formed is strongly heated till it is completely converted into cupric oxide.



The difference between the weight of cupric oxide formed and that of copper taken gives the weight of oxygen which has combined with the metal. Therefore, according to the definition

$$\text{equivalent weight of copper} = \frac{\text{Wt. of copper taken} \times 8.0}{\text{Wt. of oxygen combined}}$$

Procedure : A clean and dry porcelain crucible with its lid is accurately weighed. A few pieces of pure copper foil are put into the crucible which is weighed again with its lid. Now, concentrated nitric acid is added drop by drop to the copper foil till the metal is fully dissolved. Copper reacts vigorously with nitric acid forming copper nitrate solution and evolving brown fumes. During the

reaction, the crucible is nearly kept covered. The solution is then carefully evaporated to dryness on the waterbath so that there is no loss of solution by spitting. The green residue left after evaporation is copper nitrate. The crucible is then placed on a clay-pipe triangle and heated strongly when copper nitrate is completely converted into black cupric oxide. While heating, the lid is slightly put on one side in order that the evolved gases might escape. The reaction is complete when the evolution of brown fumes has ceased. Then the crucible with its lid and copper oxide is cooled in a desiccator and weighed again. The process of heating, cooling and weighing is repeated till the weight of the crucible is constant.

Calculations : Let

wt. of the crucible with its lid = W gms.

wt. of the crucible with its lid + copper - W_1 gms.
$$\therefore \text{Wt. of copper taken} = (W_1 - W) \text{ gms.}$$

Wt. of the crucible with lid and cupric oxide = W_2 gms.

$$\therefore \text{Wt. of combined oxygen} = (W_2 - W) - (W_1 - W) \text{ gms.} \\ = (W_2 - W_1) \text{ gms.}$$

$\therefore (W_2 - W_1)$ gms of oxygen combine with $(W_1 - W)$ gms of copper

$$\therefore 8 \quad " \quad " \quad " \quad " \quad \frac{(W_1 - W) \times 8}{(W_2 - W_1)} \quad " \quad "$$
$$\therefore \text{Equivalent weight of copper} = \frac{(W_1 - W) \times 8}{(W_2 - W_1)}$$

(C) **Method based on reduction of an oxide (Replacing oxygen from an oxide):** This method is applicable for determining the equivalent weight of metals like copper, lead, iron etc.

A weighed quantity of a metallic oxide is reduced to the metal by heating in a current of hydrogen.

$\text{CuO} + \text{H}_2 = \text{Cu} + \text{H}_2\text{O}$; $\text{PbO} + \text{H}_2 = \text{Pb} + \text{H}_2\text{O}$. By calculating the weight of combined oxygen from the difference between the weight of the oxide taken and the weight of the metal obtained after reduction, the equivalent weight of the metal can be determined as before.

*** Equivalent weight of copper :** The weight of a clean and dry porcelain boat is taken. A small quantity of dry cupric oxide is put into the boat which is weighed again. The boat with its content (CuO) is then placed in a combustion tube and heated strongly in a current of hydrogen. At the high temperature, hydrogen reduces the oxide to red metallic copper.

After the completion of the reaction, the tube is allowed to cool while the flow of hydrogen is continued for some time. When cooled to the room temperature, the boat containing the metallic copper is taken out and weighed.

Alternatively,

Let the equivalent weight of silver be x

Then, equivalent weight of silver chloride = $x + 35.46$

\therefore 1 gm.-equivalent of silver produces 1 gm.-equivalent of silver chloride

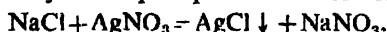
$$\frac{\text{Wt. of silver taken}}{\text{Wt. of silver chloride produced}} = \frac{\text{Eq. wt. of silver}}{\text{Eq. wt. of silver chloride}}$$

$$\frac{W}{W_1} = \frac{x}{x + 35.46}$$

The value of x is then found out.

N. B. The equivalent weight of chlorine can be determined by this process if the eq. wt. of silver is known.

(b) **Equivalent weight of sodium:** A weighed quantity of dry and pure sodium chloride is taken in a clean beaker and is dissolved completely in distilled water. The solution is made slightly acidic by adding dilute nitric acid and a dilute solution of silver nitrate is then added slowly to it in a little excess with constant stirring with a glass rod. A curdy white precipitate of silver chloride is formed.



When further addition of silver nitrate solution forms no more precipitate, the content of the beaker is slightly heated and filtered through a previously weighed filter paper. The precipitated silver chloride on the filter paper is repeatedly washed with cold water. It is then dried in an air-oven at 130°C. On cooling, the filter paper with the precipitate is weighed. The processes of heating, cooling and weighing are repeated till a constant weight is obtained.

Calculation: Let the wt. of sodium chloride = W gms.

Wt. of silver chloride produced = W_1 gms.

(107.88 + 35.46) or 143.34 gms of silver chloride contain 35.46 gms of chlorine

$$\therefore W_1 \text{ gms of silver chloride contain } \frac{35.46 \times W_1}{143.34} \text{ or } W_2 \text{ gms (say) of chlorine}$$

The same amount of chlorine is present in W gms. of sodium chloride

$$\therefore \text{Wt. of sodium in } W \text{ gms of sodium chloride} = (W - W_2) \text{ gms.}$$

W_2 gms of chlorine combine with $(W - W_2)$ gms of sodium

$$\therefore 35.46 \text{ " " " " } (W - W_2) \times 35.46$$

W_2 gms of sodium

$$\therefore \text{Equivalent weight of sodium} = \frac{(W - W_2) \times 35.46}{W_2}$$

The alternative method of calculation : Let the equivalent weight of sodium be E . Then,

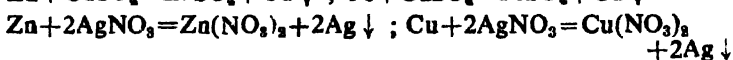
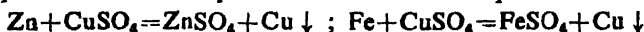
$$\frac{\text{Wt of sodium chloride taken } (W_{\text{NaCl}})}{\text{Wt. of silver chloride produced } (W_{\text{AgCl}})} = \frac{E + 35.46}{107.88 + 35.46}$$

$$\text{or, } E = \left(143.43 \times \frac{W_{\text{NaCl}}}{W_{\text{AgCl}}} \right) - 35.46$$

The equivalent weight of potassium can also be determined by application of the above method.

It is difficult to get sodium or potassium in the pure and dry state. These metals burn spontaneously in wet air. So, their equivalent weights are determined by the indirect method stated above. This method is also applicable in determining the equivalent weight of calcium.

(E) Method based upon replacement of a metal by another metal : It is an established fact that a more electropositive metal displaces a less electropositive metal from its aqueous salt solution.



It is further known that this type of displacement occurs in equivalent amounts. Let x stand for the weight of the displacing metal (A) and y for that of the metal displaced (B), then

$$\frac{x}{y} = \frac{E_A}{E_B} \quad (\text{where } E_A \text{ and } E_B \text{ are the equivalent weights of the metals A and B respectively}).$$

Therefore, if the equivalent weight of any one of the two metals is known, the equivalent weight of the other can easily be calculated.

Equivalent weight of zinc (By metal-displacement method) : A weighed quantity of pure zinc foil is added to an excess of aqueous copper sulphate solution taken in a beaker. Zinc gradually goes into the solution and red, heavy copper powder deposits at the bottom of the beaker. The reaction is complete on slight warming. When the zinc foil completely dissolves, the solution is filtered carefully through a previously weighed filter paper. The copper powder collected on the filter paper is washed thoroughly with hot water until the washing is no longer blue in colour. Copper powder is next washed twice or thrice with alcohol. The filter paper with its content (i.e. copper) is then dried in an air-oven, cooled in a desiccator and weighed. The processes of heating, cooling and weighing are repeated till there is no difference between the two subsequent weights.

Calculation : Let

wt of zinc taken = W gms

wt of copper + filter paper = W_1 gms

wt of filter paper = W_2 gms

\therefore wt of copper deposited $= (W_1 - W_2)$ gms. Now taking the equivalent weight of copper as 31.78.

$(W_1 - W_2)$ gms of copper are displaced by W gms of zinc.

\therefore 31.78 " " " " " $\frac{W \times 31.78}{(W_1 - W_2)}$ gms of zinc

\therefore Eq. wt. of zinc $\frac{W \times 31.78}{(W_1 - W_2)}$.

It is to be noted that if the equivalent weight of zinc is known, eq. wt. of copper can be found out by the above method.

Electrolytic method for determining the equivalent weight has been described in Part II of this book.

The relation between equivalent weight and atomic weight : The following simple relationship exists between the equivalent weight and the atomic weight of an element.

Let the atomic wt of an element $= A$,

the equivalent wt of the element $= E$

and the valency of the element $= V$

Then, by definition of valency,

V atoms of hydrogen combine with 1 atom of the element.

$\therefore V \times 1.008$ parts by wt. of hydrogen combine with A parts by wt. of the element.

$\therefore 1.008$ parts by wt. of hydrogen combine with $\frac{A}{V}$ parts by wt of the element.

Hence, according to definition,

equivalent weight of the element, $E = \frac{A}{V}$ or $A = E \times V$.

\therefore Atomic weight $=$ equivalent weight \times valency

This relation indicates that the atomic weight of an element is the same as its equivalent weight when the valency of the given element is 1. Thus, the atomic weights of the monovalent elements like sodium, potassium, silver, chlorine, bromine etc. coincide respectively with their equivalent weights. The atomic weight of a bivalent element (like magnesium, calcium etc) is twice its equivalent weight and atomic weight of a tri-valent element like aluminium equals to its equivalent multiplied by 3.

Since the valency is always a small whole number, the atomic weight of an element is a simple multiple of its equivalent weight.

It has already been mentioned that equivalent weight of an element is not always constant and an element may have more than one equivalent weight. We know that

(B) By the application of Dulong and Petit's law.

(C) By the application of Mitscherlich's law of isomorphism.

(A) **Cannizzaro's method** : This method of determining the atomic weight of an element which can form a large number of stable gaseous or volatile compounds has already been described earlier.

(B) **The method based on Dulong and Petit's law** : The product of the atomic weight and the specific heat of an element is called the atomic heat. Dulong and Petit after having performed a large number of experiments proved that the atomic heat of the solid elements are nearly the same and approximately equal to 6.4 at ordinary temperature. This is known as Dulong and Petit's law.

In other words, the law states that for any solid element, the product of the atomic weight and the specific heat is nearly constant and numerically equal to 6.4 (approx) at the ordinary temperature.

Atomic weight \times specific heat = Atomic heat = 6.4 (approx.)

$$\therefore \text{Atomic weight} = \frac{6.4}{\text{Specific heat}}$$

It is evident that the relation is only approximate and thus an approximate value of the atomic weight of an element can be found out if its specific heat is known.

Limitations : (i) This method of estimation of approximate atomic weights applies to solid elements only and is obviously inapplicable to liquid or gaseous elements

(ii) For certain solid elements like carbon, boron, silicon, beryllium, the atomic heat is considerably less than the expected values at the ordinary temperature. Therefore, Dulong and Petit's law does not hold true in the cases of these solid elements. In spite of these limitations, this method is frequently used as the approximate atomic weights determined can be converted into the exact values with the aid of the following relationship :

Atomic wt \div Valency \propto Equivalent wt We shall discuss the detailed calculation presently.

(B) By the application of Mitscherlich's law of isomorphism :

Isomorphous compounds and isomorphism : Chemical compounds having the same crystalline structure and exhibiting similarity in composition are said to be *isomorphous* with one another and the phenomenon of occurrence of different chemical substances in the same crystalline form is termed as *isomorphism*. However, the reverse is not necessarily true as the substances possessing similar crystalline structure may not be isomorphous in all cases.



Fig. 124 Isomorphous crystals

In addition to the identity of crystalline structure, the compounds to be isomorphous must satisfy the following conditions.

(i) *Possession of analogous formulae*: Two isomorphous compounds should have similar formulae consisting of the same number of atoms united in the same way.

(ii) *Formation of mixed crystals*: A solution containing two or more isomorphous substances on cooling separates out homogeneous crystals which contain all the substances, in varying proportions depending on the composition of the solution. Such crystals are known as mixed crystals or solid solutions.

(iii) *Formation of overgrowth*: When a crystal of a substance is kept suspended in a saturated solution of its isomorph, the suspended crystal begins to grow in size due to deposition of the latter on its surface. This phenomenon is referred to as formation of overgrowth.

A few common groups of isomorphous compounds are given below. The key elements (the elements which are different) in each group have been underlined:

(1) Zinc sulphate ($\underline{\text{Zn}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$), magnesium sulphate ($\underline{\text{Mg}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$) and ferrous sulphate ($\underline{\text{Fe}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$).

(2) Copper sulphide ($\underline{\text{Cu}}_2\text{S}$) and silver sulphide ($\underline{\text{Ag}}_2\text{S}$)

(3) Potassium sulphate ($\underline{\text{K}}_2\text{SO}_4$) and potassium chromate ($\underline{\text{K}}_2\text{CrO}_4$)

(4) Potassium permanganate ($\underline{\text{KMnO}}_4$) and potassium perchlorate ($\underline{\text{KClO}}_4$)

(5) Potash alum [$\underline{\text{K}}_2\text{SO}_4, \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$] and chrome alum [$\underline{\text{K}}_2\text{SO}_4, \underline{\text{Cr}}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$]

Since zinc sulphate, magnesium sulphate and ferrous sulphate are isomorphous substances, they exhibit identity of crystalline forms. When a solution containing zinc sulphate and magnesium sulphate (or ferrous sulphate) is allowed to crystallise, homogeneous crystals known as mixed crystals which contain both the sulphates of magnesium and zinc (or of iron) will separate out. Further, if a crystal of zinc sulphate be placed in a saturated solution of magnesium sulphate (or of ferrous sulphate), magnesium sulphate (or ferrous sulphate) continues to deposit on the crystal of zinc sulphate.

From the formulae of the above substances, it becomes evident that each of the molecules of two isomorphous compounds contains equal number of atoms united in the same manner. More clearly, the same number of similarly arranged atoms of the key elements and the remaining identical elements constitute the molecules of the isomorphous substances. Thus, the only difference in the molecules of isomorphous sulphates of zinc, magnesium and iron is that

in place of zinc in the first one, we have magnesium in the second and iron in the third.

It has now been realised that the phenomenon of isomorphism depends more on the similarity in the geometrical forms of the crystals rather than the similarity in chemical properties.

Law of isomorphism and determination of atomic weight :

From the examination of a large number of isomorphous compounds, Mitscherlich formulated a law which states,

The equal number of atoms united in the same fashion produce the isomorphous crystals. This is known as *Mitscherlich's law of isomorphism*. This law leads to the concept that crystalline form of a substance depends essentially upon the number of constituent atoms and the way in which they are combined and is independent of its chemical nature. In other words, the law of isomorphism may be stated as—the isomorphous compounds i.e. the compounds having similar crystalline forms and usually similar chemical characteristics can be represented by similar formulae which contain the same number of atoms (chemically similar or dissimilar) united in the same manner. A critical study reveals that in isomorphous compounds two analogous elements (chemically similar) replace each other, atom for atom, without disturbing the crystalline structures. Moreover, the weights of two elements replacing each other are in the ratio of their atomic weights. These facts are utilised in the determination of the atomic weight of either of the two replacing elements.

Let A and B be two analogous elements present in a pair of isomorphous compounds and let a and b be the atomic weights of A and B respectively. Let us further suppose that W_1 gms of A in one compound replace W_2 gms of B from the other compound.

Then,

the number of atoms of A = $\frac{W_1}{a}$, and

the number of atoms B = $\frac{W_2}{b}$

We know that one atom of A will replace one atom of B.

\therefore Number of atoms of replacing element (A) = Number of atoms of element replaced (B).

Therefore, $\frac{W_1}{a} = \frac{W_2}{b}$ or $\frac{W_1}{W_2} = \frac{a}{b}$

That is to say,

$\frac{\text{wt. of the element A}}{\text{wt. of the element B}} = \frac{\text{atomic weight of A}}{\text{atomic weight of B}}$

So, if the weights of the two interchangeable elements are determined accurately and the atomic weight of one of the two elements is known, we can easily calculate the atomic weight of the other element from the above relationship.

It follows directly from the law of isomorphism that in a group of two isomorphous compounds, elements substituting each other should have the same valency. So if the valency of one element is known, the valency of the other is automatically decided. For example, zinc oxide is isomorphous with beryllium oxide. The formula of zinc oxide is ZnO and the valency of zinc is 2. Therefore, according to the law of isomorphism, the valency of beryllium must be 2 and beryllium oxide must have the formula BeO . The application of the knowledge of valency in determining the exact atomic weight of an element will be discussed later.

N. B. (a) A crystal of sodium chloride and that of a diamond have identical geometrical forms but these substances are not isomorphous because they fail to satisfy the other conditions of isomorphism.

(b) Many cases are known where substances with similar formulae and chemical properties are not isomorphous e.g. sodium nitrate (NaNO_3) and potassium nitrate (KNO_3). In certain cases, isomorphism is found amongst chemically similar substances having dissimilar formulae differing in the number of atoms in the molecules. For example, Ag_2S is isomorphous with PbS ; K_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ are isomorphous substances.

(c) Compounds having the same number of atoms of entirely different chemical character are sometimes found to be isomorphous. Thus, NaNO_3 and CaCO_3 ; KMnO_4 and BaSO_4 are two pairs of isomorphous compounds.

Determination of exact atomic weights: We know that the product of the equivalent weight and the valency of an element is numerically equal to its atomic weight. i.e.,

Atomic weight = Equivalent weight \times Valency. The exact atomic weight of an element is found out from the above relationship and the steps to be followed in the method are given below ;

Step—I. The accurate equivalent weight of the element under consideration is determined by a chemical method.

Step—II. There is no reliable method by which valency of the element could be derived with accuracy, it is obtained indirectly from the relation—

$$\text{Valency} = \frac{\text{Atomic weight}}{\text{Equivalent weight}}.$$

The approximate value of the atomic weight determined by the method based on Dulong and Petit's law or by any other suitable method is then divided by the equivalent weight. The valency thus obtained is changed to the nearest whole number (since valency of an element can never be a fraction).

Step—III. Finally, the equivalent weight is multiplied by the valency in order to get the exact atomic weight.

Numerical problems

On the equivalent weight :

(1) 1.8 gms. of magnesium were completely converted into its oxide and the weight of the oxide formed was 3.008 gms. What is the equivalent weight of magnesium ?

Wt. of magnesium oxide = 3.008 gms.

Wt. of magnesium = 1.8 gms

Wt. of combined oxygen = (3.008 - 1.8) or 1.208 gms.

Now, 1.208 gms. of oxygen combine with 1.8 gms. of magnesium

∴ 8 " " " " " " $\frac{1.8 \times 8}{1.208}$ " " "

So, the equivalent weight of magnesium = $\frac{1.8 \times 8}{1.208} = 11.92$

(2) 0.981 gm of a metal may be converted to 2.046 gms of its chloride. Calculate the equivalent weight of the metal. (Cl = 35.5)

Weight of the chloride = 2.046 gms

" " " metal = 0.981 gm.

" " combined chlorine = 2.046 - 0.981 = 1.065 gms

1.065 gms of chlorine combine with 0.981 gm of the metal

35.5 " " " " " " $\frac{0.981 \times 35.5}{1.065}$ gms of the metal

∴ Equivalent weight of the metal = $\frac{0.981 \times 35.5}{1.065} = 32.7$

(3) A current of pure and dry hydrogen was passed over 0.8567 gm of heated pure black oxide of copper till the reaction was complete. On passing the gaseous product formed through a previously weighed tube containing fused calcium chloride, the gain in weight of the tube was 0.1941 gm. What is the equivalent weight of copper ? [At. wt. of hydrogen = 1]

Hydrogen reduces the heated copper oxide to metallic copper and is itself oxidised to steam which on the other hand is absorbed in the CaCl_2 -tube.

∴ The gain in weight of calcium chloride-tube

= The weight of steam (or water) formed = 0.1941 gm

18 gms of water contain 16 gms of oxygen

∴ 0.1941 gm " " contains $\frac{0.1941 \times 16}{18}$ or 0.1725 gm of

oxygen

∴ Wt. of oxygen present in the given quantity of copper oxide = 0.1725 gm

∴ Wt. of copper = (0.8567 - 0.1725) = 0.6842 gm

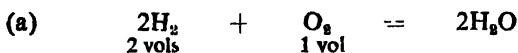
Now, 0.1725 gm of oxygen is combined with 0.6842 gm of copper

$$\therefore 8 \text{ gms } \text{O}_2 \text{ are } \frac{0.6842 \times 8}{0.1725} \text{ gms of copper}$$

$$\therefore \text{Equivalent weight of copper} = \frac{0.6842 \times 8}{0.1725} = 31.73$$

(4) (a) The volume of dry hydrogen obtained at N.T.P. by dissolving 0.109 gm of a metal in dil. acid was found to combine completely with 37.5 c.c of oxygen. Determine the equivalent weight of the metal.

(b) On dissolving 2.0 gms of a metal in sulphuric acid, 4.51 gms of the metal sulphate was formed. What is the equivalent weight of the metal?



Hence, the volume of hydrogen required to combine with oxygen = $37.5 \times 2 = 75$ c.c. = volume of hydrogen evolved at N.T.P.

$$\text{Again, weight of the same volume of hydrogen} = 75 \times 0.00009 \text{ gm} = 0.00675 \text{ gm}$$

\therefore 0.00675 gm of hydrogen is displaced by 0.109 gm of metal

$$\therefore 1.008 \text{ gms } \text{H}_2 \text{ are } \frac{0.109 \times 1.008}{0.00675} \text{ gms of the metal}$$

$$\therefore \text{Equivalent weight of the metal} = \frac{0.109 \times 1.008}{0.00675} = 16.27$$

$$(b) \text{ Equivalent weight of the sulphate radical} = \frac{48}{2} = 48$$

Now, (4.51 - 2) or 2.51 gms of sulphate radical combines with 2 gms of the metal

\therefore 48 gms of sulphate radical combine with $\frac{2 \times 48}{2.51}$ gms of the metal.

$$\therefore \text{Eq. wt. of the metal} = \frac{2 \times 48}{2.51} = 38.247$$

(5) The solution obtained by dissolving 1.201 gms of zinc in nitric acid was evaporated to dryness. The solid residue on strong heating produced 1.497 gms of zinc oxide. In another experiment, 0.543 gm of zinc displaced 0.527 gm of copper from a solution of copper sulphate. Find the equivalent weights of zinc and copper.

$$\text{Wt. of zinc} = 1.201 \text{ gms ; wt of zinc oxide} = 1.497 \text{ gms}$$

$$\therefore \text{Wt of combined oxygen} = 1.497 - 1.201 = 0.296 \text{ gm}$$

0.296 gm of oxygen combines with 1.201 gms of zinc

$$\therefore 8 \text{ gms } \therefore \text{ combine } \therefore \frac{1.201 \times 8}{0.296} \therefore \therefore$$

$$\therefore \text{Equivalent weight of zinc} = \frac{1.201 \times 8}{0.296} = 32.45$$

We know that when a metal displaces another metal from the solution of a salt of the latter, the displacement takes in the ratio of the chemical equivalents of the two metals.

$$\therefore \frac{\text{Wt of zinc (the displacing metal)}}{\text{Wt of copper (the metal displaced)}} = \frac{\text{Eq. wt of zinc}}{\text{Eq. wt of copper}}$$

$$\therefore \frac{0.443}{0.527} = \frac{32.45}{\text{Eq. wt of copper}}$$

$$\therefore \text{Eq. wt. of copper} = \frac{32.45 \times 0.527}{0.443} = 31.5$$

(6) 0.1827 gm of the chloride of a metal was converted quantitatively into 0.1057 gm of the corresponding oxide. Calculate the equivalent weight of the metal. (Cl=35.5).

If x be the eq. wt. of the metal, $(x+8)$ gms of the oxide will be obtained from $(x+35.5)$ gms of the chloride ($\therefore 8$ and 35.5 are the eq. wts of oxygen and chlorine respectively)

$$\therefore \frac{x+8}{x+35.5} = \frac{0.1057}{0.1827}$$

$$\therefore x = 29.88 \text{ i.e. Eq. wt of the metal} = 29.88$$

(7) A solution containing 1 gm of zinc chloride gave 2.110 gms of silver chloride on treatment with excess of silver nitrate solution. Calculate the equivalent weight of zinc (Ag=107.88, Cl=35.46, valency of Ag=1)

107.88 + 35.46 or 143.34 gms of silver chloride contain 35.46 gms of chlorine.

$$\therefore 2.110 \text{ gms of silver chloride contain } \frac{35.46 \times 2.110}{143.34} \text{ or } 0.5219 \text{ gm of chlorine}$$

\therefore Wt of chlorine present in the given quantity of zinc chloride = 0.5219 gm

Wt of zinc $(1 - 0.5219) = 0.4781$ gm

0.5219 gm of chlorine combines with 0.4781 gm of zinc

$$\therefore 35.46 \text{ gms } \therefore \therefore \text{ combine } \therefore \frac{0.4781 \times 35.46}{0.5219}$$

gms of zinc

$$\therefore \text{Eq. wt of zinc} = \frac{0.4781 \times 35.46}{0.5219} = 32.48$$

Alternatively, let x be the equivalent weight of zinc

$$\text{Then, } \frac{\text{wt of zinc chloride}}{\text{wt of silver chloride}} = \frac{x + 35.46}{107.88 + 35.46}$$

$$\text{or, } \frac{1}{2.110} = \frac{x + 35.46}{143.34} \quad \therefore x = 32.48$$

Problems on the atomic weights of elements :

(8) The chloride of a metal was found to contain 20.2% chlorine. The specific heat of the metal was 0.224. Calculate the exact atomic weight of the metal. Write down the molecular formula of the chloride of the metal. (Cl = 35.5)

As per data given,

in 100 gms. of the metal chloride

wt. of the metal = 20.2 gms.

\therefore wt. of chlorine = $(100 - 20.2) = 79.8$ gms.

79.8 gms of chlorine combine with 20.2 gms. of the metal,

\therefore 35.5 " " " " " $\frac{20.2 \times 35.5}{79.8}$ gms. of the metal

\therefore Eq. wt of the metal = $\frac{20.2 \times 35.5}{79.8} = 8.98$.

Applying Dulong and Petit's law,

approx. atomic weight of the metal = $\frac{6.4}{0.224} = 28.57$

\therefore Valency of the metal = $\frac{28.57}{8.98} = 3.18 \approx 3$ (nearest whole number)

\therefore Exact at. wt. of the metal = $8.98 \times 3 = 26.94$

If the metal is symbolised by M, the molecular formula of its chloride is MCl_3

(9) If the equivalent weight of a metal (M) be x and the formula of its oxide be M_mO_n , show the atomic weight of

$$M = \frac{2xn}{m} \quad [\text{W. B. H. S. 1983}]$$

From the formula of the oxide M_mO_n , it is evident that

16n gms. of oxygen combine with am gms. of M where
 $a = \text{at. wt. of M}$

\therefore 8 gms. of oxygen combine with $\frac{am \times 8}{16n} = \frac{am}{2n}$ gms. of M

\therefore x or eq. wt. of $m = \frac{am}{2a}$ or $a = \frac{2xn}{m}$

Alternatively,

From the formula of the oxide M_nO_m , it is seen that

m atoms of M combine with n atoms of oxygen

\therefore 1 atom „ „ combines „ $\frac{n}{m}$ „ „ „

$\frac{n}{m}$ atoms of oxygen $\equiv \frac{2n}{m}$ atoms of hydrogen

\therefore valency of $M = \frac{2n}{m}$

\therefore At. wt. of $M = \frac{2xn}{m}$.

(9a) A metal forms a solid oxide containing 34.8% of oxygen. The atomic weight of the metal is 45. Calculate the valency of the metal and write down the formula of its oxide.

In the oxide,

percentage of oxygen = 34.8

\therefore „ „ metal = $(100 - 34.8) = 65.2$

34.8 parts by wt of oxygen combine with 65.2 parts by wt of the metal

\therefore 8 „ „ „ „ „ „ „ $\frac{65.2 \times 8}{34.8}$ parts by wt of the metal.

\therefore Eq. wt. of the metal = $\frac{65.2 \times 8}{34.8} = 14.9$

\therefore Valency of the metal = $\frac{\text{At. wt.}}{\text{Eq. wt.}} = \frac{45}{14.9} = 3$ (nearest whole number)

\therefore Formula of the metallic oxide = M_2O_3 (where M stands for the symbol of the metal.)

(10) 0.1 gm. of a metal (M) when dissolved in dilute hydrochloric acid gave 124.4 c.c. of dry hydrogen at N.T.P. The specific heat of the metal is 0.214. What is the accurate atomic weight of the metal? Write down the formulas of the oxide, chloride and phosphate of the metal.

Wt. of 1 c.c. of hydrogen at N.T.P. = 0.00009 gms.

\therefore wt of 124.4 c.c. of „ „ „ = 124.4×0.00009 gms.
 ≈ 0.0112 gm.

\therefore 0.0112 gm. of hydrogen is displaced by 0.1 gm of the metal

\therefore 1.008 gms. „ „ are „ „ $\frac{0.1 \times 1.008}{0.0112}$ of the metal.

\therefore Eq. wt of M = $\frac{0.1 \times 1.008}{0.0112} = 9$

According to Dulong and Petit's law, approx. at. wt. = $\frac{6.4}{0.214} = 29.9$

\therefore Valency = $\frac{29.9}{9} = 3.32 \approx 3$ (nearest whole number)

\therefore Accurate at. wt. of M = $9 \times 3 = 27$ and the formulas of the oxide, chloride and phosphate are M_2O_3 , MCl_3 and MPO_4 respectively.

(11) An oxide of an element contains 53% of the element. The vapour density of the chloride of the element is 66. Calculate the atomic weight of the element. (Cl = 35.5)

In the oxide,

percentage of the element = 53 ; percentage of oxygen = $\frac{100 - 53}{= 47}$

Hence,

47 parts by wt. of oxygen combine with 53 parts by wt. of the element

\therefore 8 „ „ „ „ „ „ $\frac{53 \times 8}{47}$ „ „ „ „

\therefore Eq. wt of the element = $\frac{53 \times 8}{47} = 9.02$

Vapour density of the chloride of the element = 66

\therefore Mol. wt. „ „ „ „ „ „ = $2 \times 66 = 132$
(according to Avogadro)

Let the valency of the element = V, its at. wt. = A and its symbol = M, then

the formula of the chloride will be MCl_V

\therefore Mol. wt. of the chloride = $A + 35.5V$
= $EV + 35.5V$ [\because at. wt. = eq. wt (E) \times valency]
= $V(E + 35.5) = V(9.02 + 35.5) = 44.52V$

Now, $44.52V = 132$, $\therefore V = \frac{132}{44.52} = 3$ (nearest whole number)

\therefore At. wt of the element = $9.02 \times 3 = 27.06$

(12) The equivalent weight of a metal is 29.73 and the vapour density of its chloride is 16.30 (O = 1). Find out the atomic weight of the metal.

Vapour density of the metallic chloride (given) = 16.30 (O = 1)

The vapour density of oxygen = 8 (H = 1)

\therefore actual vapour density of the metallic chloride = $16.30 \times 8 = 130.40$

\therefore Mol. wt. of the metallic chloride = $2 \times 130.40 = 260.80$

Let the formula of the chloride be MCl_v (where M = symbol of the metal, v = valency of the metal)

\therefore Mol. wt. of the chloride = At. wt. of M + $35.5v$

or, $260.80 = 29.73 \times v + 35.5v$ (\therefore At. wt = Eq. wt \times valency)

$\therefore v = 4$ (nearest whole number)

\therefore At. wt. of the element = $29.73 \times 4 = 118.92$

(13) Potassium permanganate is isomorphous with potassium perchlorate ($KClO_4$). Analysis shows that potassium permanganate contains 34.8% of manganese. Find the atomic weight of manganese.

Let x be the at. wt. of manganese. \therefore The formula of potassium permanganate is $KMnO_4$ as it is isomorphous with $KClO_4$.

So, the molecular wt. of $KMnO_4 = 39 + x + 4 \times 16 = 103 + x$

and % of Mn in the compound = $\frac{x \times 100}{103 + x}$

\therefore According to data supplied,

$$\frac{x \times 100}{103 + x} = 34.8 \quad \therefore x = 54.98$$

(14) A metal M forms a chloride which contains 70.66% by weight of the metal and is isomorphous with KCl. Calculate the atomic weight of the metal (Cl = 35.5).

In 100 parts by weight of the given chloride

wt. of the metal = 70.66 parts

wt. of chlorine = $100 - 70.66 = 29.34$ parts

29.34 parts by wt. of chlorine combine with 70.66 parts by wt. of the metal

$$\therefore 35.5 \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \frac{70.66 \times 35.5}{29.34}$$

parts by wt. of the metal

$$\therefore \text{Eq. wt. of the metal} = \frac{70.66 \times 35.5}{29.34} = 85.49$$

Chloride of M is isomorphous with KCl

\therefore Valency of M will be equal to that of potassium i.e. 1

\therefore At. wt. of M = $85.49 \times 1 = 85.49$

Alternatively,

In the chloride of M,

29.34 gms of chlorine combine with 70.66 gms of the metal

\therefore 1 gm „ „ combines with $\frac{70.66}{29.34}$ or 2.40 gms of the metal

In potassium chloride

35.5 gms of chlorine are in combination with 39 gms of potassium

\therefore 1 gm „ is „ „ $\frac{39}{35.5}$ or 1.09 gms of potassium

So in the two isomorphous compounds, the ratio of the weights of metal and potassium combining with the same weight of chlorine = 2.40 : 1.09

But in the two compounds, the number of atoms of the metal = number of atoms of potassium i.e. the ratio between the weights of M and potassium is equal to that between the atomic wts of M and potassium.

$$\therefore \frac{\text{At. wt of M}}{\text{At. wt of potassium}} = \frac{2.40}{1.09}$$

$$\therefore \text{At. wt of M} = \frac{2.40 \times 39}{1.09} \text{ or } 85.8$$

(\because at. wt. of potassium = 39)

(15) The oxides of the metals A and B are isomorphous. The atomic weight of A is 43.5 and the vapour density of its chloride is 75. The oxide of the metal B contains 40% of oxygen. Calculate the atomic weight of B. (Cl = 35.5)

Mol. wt of the chloride of the metal A = $2 \times 75 = 150$

(according to Avogadro's hypothesis)

Let the valency of A be V. Then the formula of its chloride will be ACl_V

$$\therefore \text{Mol. wt. of the chloride} = 150 = (43.5 + 35.5V)$$

$$\therefore V = \frac{150 - 43.5}{35.5} \text{ or } 3 \text{ (nearest whole number)}$$

So, the formula of the oxide of A = A_2O_3 .

Again, in the oxide of B

Percentage of oxygen = 40.0

$$\therefore \text{ „ „ the metal B} = 100 - 40 = 60$$

40 parts by weight of oxygen combine with 60 parts by weight of B

\therefore 8 " " " " " combine with $\frac{60 \times 8}{40}$

or 12 parts by weight of B

\therefore Eq. wt of B = 12. Since the oxide of B is isomorphous with that of A, the formula of the oxide of B will be B_2O_3 and the valency of B is 3.

\therefore At. wt of B = $12 \times 3 = 36$

(16) 0.12 gm of a metal is dissolved completely in dilute sulphuric acid liberating 41.10 ml of hydrogen at N.T.P. Calculate the equivalent weight of the metal. The residue left gave on evaporation in a desiccator a white crystalline compound isomorphous with $FeSO_4 \cdot 7H_2O$. Molecular weight of the compound was approximately 287. Calculate the exact atomic weight of the metal. [Use the data : gram-molecular volume of a gas is 22.4 litres at N.T.P. and atomic weight of sulphur is 32]

1 gm-molecule of hydrogen = $2 \times 1.008 = 2.016$ gms of hydrogen.
41.10 ml of hydrogen = 0.0411 litre of hydrogen.

At N.T.P., 22.4 litres of hydrogen weigh 2.016 gms

\therefore " " " 0.0411 " " weighs $\frac{2.016 \times 0.0411}{22.4}$ gms

Now, $\frac{2.016 \times 0.0411}{22.4}$ gms of hydrogen are displaced by 0.12 gm of metal

\therefore 1.008 " " " $\frac{22.4 \times 0.12 \times 1.008}{2.016 \times 0.0411}$ gms of metal

\therefore Eq wt of the metal = $\frac{22.4 \times 0.12 \times 1.008}{2.016 \times 0.0411} = 32.7$

Since the sulphate obtained by dissolving the metal in dil. sulphuric acid is isomorphous with $FeSO_4 \cdot 7H_2O$, it contains the same number of atoms united in the same way. So its formula will be $MSO_4 \cdot 7H_2O$ (where M represents the metal) and the valency of the metal is 2.

Let the atomic weight of the metal be x

\therefore Molecular weight of $MSO_4 \cdot 7H_2O = x + 32 + 4 \times 16 + 7 \times 18 = x + 222$

\therefore $x + 222 = 287$ or $x = 65 =$ At wt of the metal (approx)

Again, valency = $\frac{\text{At. wt}}{\text{Eq. wt}} = \frac{65}{32.7} = 2$ (nearest whole number)

\therefore Exact at. wt. of the metal = $32.7 \times 2 = 65.4$

(17) Magnesite and calamine are isomorphous and percentages of magnesium and zinc in the salts are 28.57 and 52 respectively. The atomic weight of zinc being 65, calculate that of magnesium.

Magnesite and calamine possess the similar formulae as they are isomorphous. So the weights of magnesium and zinc which have combined with the same weight of carbonate radical are in the ratio of their atomic weights.

Percentage of magnesium in magnesite = 28.57

„ „ carbonate „ = 100 - 28.57 = 71.43
 „ „ zinc in calamine = 52
 „ „ carbonate „ = 100 - 52 = 48

wt. of magnesium which combines with 48 parts by weight of carbonate radical = $\frac{28.57}{71.43} \times 48 = 19.2$

In two isomorphous compounds, the ratio of the weights of magnesium and zinc that combine with the same wt. of CO_3 radical is 19.2 : 52 and the two compounds will contain the same number of atoms of the two metals i.e. ratio of their wts. must be the ratio of their atomic wts.

$$\therefore \frac{\text{At. wt. of magnesium}}{\text{At. wt. of zinc}} = \frac{19.2}{52}$$

Let x be the at. wt. of magnesium.

$$\therefore \frac{x}{65} = \frac{19.2}{52} \quad \therefore x = 24$$

Mole and chemical calculations using mole concept : It has been discussed earlier that the molecular weight of any substance, (element or compound) in grammes is called the gram-molecule or mole of the substance and the mole of a substance always contains a fixed number of its molecules. This fixed number is known as the Avogadro number or Avogadro constant, the accepted value of which is 6.023×10^{23} . Thus, 2.016 gms of hydrogen contain as many molecules as there are in 28.016 gms of nitrogen or 17.032 gms. of ammonia.

It has further been proved that 1 gm-atom (atomic weight expressed in grammes) of any element contains Avogadro number (6.023×10^{23}) of atoms of that element and the number of individual ions present in 1 gm-ion (relative weight of an ion expressed in grammes) of any ion is also 6.023×10^{23} . So 32.00 gms of sulphur, 12.00 gms of carbon and 22.99 grammes of sodium contain the same constant number of atoms of the respective elements and this constant number is always 6.023×10^{23} . Similarly, 22.99 gms of Na^+ , 35.46 gms of Cl^- and 96 gms of SO_4^{-2} will be found to contain 6.023×10^{23} ions of the respective species.

It may be noted that an atom or a radical by the loss or gain of one or more electrons is converted to an ion. The weights (mass) of the electrons are negligible and for all practical purposes, the weight of an ion is taken to be equal to that of an atom or a radical from which it is obtained.

In the light of Avogadro number the concept of mole is now applied in a wider sense. The 'mole' is now regarded as the amount of the substance which contains Avogadro number of elementary entities (such as molecules, atoms, ions, or electrons) constituting the substance under investigation. In other words, the fixed weight of any substance, (molecular, atomic or ionic) containing 6.023×10^{23} particles of the substance is known as the mole.

To differentiate between 1 gm-molecule, 1 gm-atom and 1 gm ion, the terms mole molecule, mole atom, mole-ion etc. are sometimes used instead of simple mole.

Nowadays, the term 'mole' is frequently used as a unit in various types of chemical calculations and in many cases, the method of calculations based on the mole concept is easier and more logical than the method commonly employed.

We know that any chemical reaction takes place in the ratio of the definite weights of the substances taking part in it. As it is possible to calculate easily how many moles of a substance correspond to a given weight (mass) of that substance, we may say that the substances react in the ratio of the definite number of moles. Thus, the number of moles of a substance and its corresponding quantity can be used synonymously.

Now, 1 mole molecule = molecular wt (in gms) ;

1 mole atom = atomic wt (in gms) ;

1 mole ion = wt of an ion (in gms)

and number of moles \times N (Avogadro Number) = Number of molecules or atoms or ions.

$$\therefore 15 \text{ gms of } \text{MnO}_2 = \frac{15}{87} \text{ or } \frac{5}{27} \text{ mole of } \text{MnO}_2$$

$$5.4 \text{ gms, aluminium} = \frac{5.4}{27} \text{ mole or } 0.2 \text{ moles of aluminium}$$

$$0.2 \text{ mole of aluminium} \times N = 0.2 \times 6.023 \times 10^{23} \text{ atoms of aluminium}$$

$$0.01 \text{ mole of sulphuric acid} = 0.01 \times 98 = 0.98 \text{ gm of sulphuric acid}$$

$$0.01 \text{ mole of sulphuric acid} \times N = 0.01 \times 6.023 \times 10^{23} \text{ molecules of sulphuric acid.}$$

We know further that 22.4 litres of any gas at N.T.P. contain one mole molecule (or one mole atom in the case of monatomic element)

$$\therefore \text{At N.T.P. } 2.8 \text{ litres of } \text{CO}_2 = \frac{2.8}{22.4} \text{ or } 0.125 \text{ mole of } \text{CO}_2$$

$$0.25 \text{ mole of } \text{SO}_2 = 0.25 \times 22.4 = 5.6 \text{ litre of } \text{SO}_2 \text{ at N.T.P.}$$

$$0.1 \text{ mole of sulphate ion } (\text{SO}_4) = 0.1 \times 96 = 9.6 \text{ gms of } \text{SO}_4 \text{ ions.}$$

0.1 mole of SO_4^- ions $\times N = 0.1 \times 6.023 \times 10^{23}$ of sulphate ions

1.773 gms of chloride ion (Cl^-) = $\frac{1.773}{35.46}$ moles or 0.05 mole of Cl^-

The term mole electron has also been introduced. The equivalent weight when expressed in grammes is referred to as the mole equivalent.

1 gm of hydrogen = 1 mole equivalent of hydrogen atoms

8 gms of oxygen = 0.5 mole equivalent of oxygen atoms

35.46 ,, ,, chlorine = 1 mole equivalent of chlorine atoms.

Numerical problems using mole concept

(1) How many grammes of carbon and oxygen are present in 2.5 moles of carbon dioxide?

Wt. of carbon in 1 mole of carbon dioxide (CO_2) = 12 gms

\therefore ,, ,, ,, ,, 2.5 moles ,, ,, ,, = 12×2.5
= 30 gms.

Wt. of oxygen in 1 mole of carbon dioxide = $16 \times 2 = 32$ gms

\therefore ,, ,, ,, ,, 2.5 moles ,, ,, ,, = 32×2.5
= 80 gms.

(2) How many atoms of hydrogen and oxygen are present in 14.4 gms of water?

14.4 gms of water = $\frac{14.4}{18}$ mole or 0.8 mole of water

Number of hydrogen atoms present in 1 mole of water
= $6.023 \times 10^{23} \times 2$

\therefore ,, ,, ,, ,, ,, ,, 0.8 mole of water
 $6.023 \times 10^{23} \times 2 \times 0.8$
= 9.636×10^{23}

Number of oxygen atoms present in 1 mole of water
= 6.023×10^{23}

\therefore ,, ,, ,, ,, ,, ,, 0.8 ,, ,, ,,
= $6.023 \times 10^{23} \times 0.8$
 4.818×10^{23}

(3) What weight of nitrogen contains the same number of molecules as 11.2 litres of carbon dioxide at N.T.P.?

11.2 litres of CO_2 = $\frac{11.2}{22.4}$ or 0.5 mole of CO_2

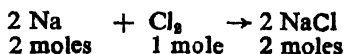
Number of molecules present in 0.5 mole of CO_2 = Number of molecules of nitrogen present in 0.5 mole of nitrogen

0.5 mole of nitrogen = $28 \times 0.5 = 14$ gms.

(4) 2.3 gms of sodium are lowered into 2000 ml bottle filled with chlorine gas at N.T.P. After the reaction is over, find—

(i) How many moles of NaCl are formed in the reaction ?

(ii) Which of the substances is left unconsumed ? Give its weight in grams. (Na=23 ; Cl=35.5)



= 22.4 litres at N.T.P.

Number of moles that have been taken = $\frac{2.3}{23} = 0.1$ mole

From the above reaction, it is seen that 2 moles of Na react with 22.4 litres of Cl_2 to form 2 moles of NaCl.

\therefore 0.1 mole of Na reacts with $\frac{22.4 \times 0.1}{2}$ or 1.12 litres or 1120 ml of Cl_2 at N.T.P. to give 0.1 mole of NaCl

As the bottle contains 2000 ml of Cl_2 at N.T.P.,

the vol. of unconsumed Cl_2 gas = 2000 - 1120

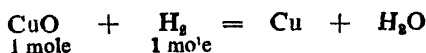
= 880 ml at N.T.P.

Now 22400 ml of Cl_2 at N.T.P. weigh $35.5 \times 2 = 71$ gms

\therefore 880 ml of Cl_2 at N.T.P. weigh = $\frac{71 \times 880}{22400}$
= 2.79 gms.

(5) A current of dry hydrogen is passed over cupric oxide heated in a bulb tube. Calculate the volume of hydrogen at N.T.P. required for the reduction of 0.8 gm of the oxide. (Cu=63.57)

0.8 gms of cupric oxide = $\frac{0.8}{79.57} = 0.01$ mole of CuO

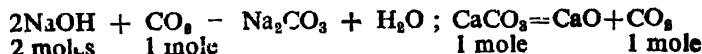


1 mole of the oxide requires 1 mole of hydrogen

\therefore 0.01 „ „ „ „ „ „ 0.01 „ „ „

0.01 mole of $\text{H}_2 = 0.01 \times 22.4 = 0.224$ litre of hydrogen

(6) What weight of calcium carbonate would produce sufficient carbon dioxide to convert 30 gm of caustic soda into sodium carbonate ? (Ca = 40, Na = 23)



2 moles of NaOH for its conversion into Na_2CO_3 require 1 mole of carbon dioxide which is obtained by heating 1 mole of CaCO_3 .

Again, 30 gms. of NaOH = $\frac{30}{40} = \frac{3}{4}$ mole of NaOH

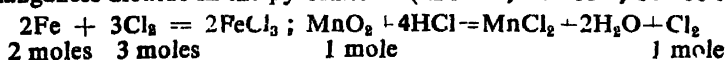
\therefore 2 moles of NaOH require 1 mole of CaCO_3

$\therefore \frac{3}{4}$ mole „ „ requires $\frac{3}{2 \times 4}$ or $\frac{3}{8}$ mole of CaCO_3

$\frac{3}{8}$ mole of $\text{CaCO}_3 = \frac{3}{8} \times 100$

= 37.5 gms. of CaCO_3 (\because mol. wt $\text{CaCO}_3 = 100$)

(7) 38.97 gms. of pyrolusite (impure manganese dioxide) liberate sufficient chlorine from hydrochloric acid to convert 10 gms. of iron to anhydrous ferric chloride. Calculate the percentage of pure manganese dioxide in the pyrolusite. (Mn = 55, Fe = 55.8, Cl = 35.5)



Now 10 gms. of iron = $\frac{10}{55.8}$ mole of iron.

From the first equation, we know

2 moles of iron require 3 moles of chlorine

$\therefore \frac{10}{55.8}$ mole „ „ requires $\frac{3 \times 10}{2 \times 55.8}$

Again from the second equation,

1 mole of chlorine is obtained from 1 mole of MnO_2

$\therefore \frac{3 \times 10}{2 \times 55.8}$ „ „ „ „ „ $\frac{3 \times 10}{2 \times 55.8}$ mole of MnO_2

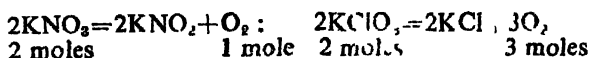
$\frac{3 \times 10}{2 \times 55.8}$ mole of $\text{MnO}_2 = \frac{3 \times 10 \times 87}{2 \times 55.8}$
= 23.387 gms. of MnO_2

Now, 38.97 gms. of pyrolusite contain 23.387 gms. of pure MnO_2

$\therefore 100$ „ „ „ „ $\frac{23.387 \times 100}{38.97}$
or 60 gms. of MnO_2

\therefore % of pure $\text{MnO}_2 = 60$.

(8) 10 gms. of each of potassium nitrate and potassium chlorate are separately decomposed to yield oxygen. Compare the volumes of oxygen produced at N.T.P. (K = 39, N = 14, Cl = 35.5)



From the above equations, it is evident that 2 moles of KNO_3 decompose to yield 1 mole of oxygen while 2 moles of KClO_3 give 3 moles of oxygen.

Now, 10 gms. of potassium nitrate = $\frac{10}{101} = 0.099$ mole of KNO_3

and 10 gms. of potassium chlorate = $\frac{10}{122.5} = 0.082$ mole of KClO_3

\therefore Oxygen produced from 0.099 mole of KNO_3
 $= \frac{1 \times 0.099}{2} = 0.0495$ mole

and " " " 0.082 mole of KClO_3
 $= \frac{3 \times 0.082}{2} = 0.1224$ mole

0.0495 mole of oxygen = $0.0495 \times 22.4 = 1.109$ litres of oxygen

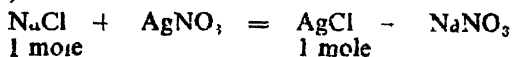
0.1224 mole " " = $0.1224 \times 22.4 = 2.742$ litres " "

\therefore Vol. of oxygen from potassium nitrate = $\frac{1.109}{2.742} = \frac{1}{2.472}$

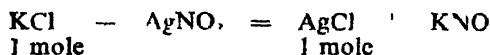
Vol. of oxygen from potassium chlorate = $\frac{2.742}{2.472}$

\therefore Ratio of the vols. of oxygen 1 : 2.472

(9) 1.2 gms. of a mixture of sodium and potassium chlorides gave with silver nitrate 2.869 gms of silver chloride. What is the weight of sodium chloride in the mixture? ($\text{Na}=23$, $\text{K}=39$, $\text{Cl}=35.5$, $\text{Ag}=108$)



1 mole 1 mole



1 mole 1 mole

From the above equations, we find that

1 mole of NaCl + 1 mole of KCl = 2 moles of AgCl

mol. wt of NaCl = $23 + 35.5 = 58.5$; mol. wt of KCl = $39 + 35.5 = 74.5$ and mol. wt of AgCl = $108 + 35.5 = 143.5$

Let x be the weight of NaCl in the mixture.

\therefore wt of KCl in the mixture $(1.2 - x)$ gms

$$\frac{x}{58.5} + \frac{1.2 - x}{74.5} = \frac{2.869}{143.5}$$

Solving the equation, we get

$x = 1.169$ \therefore Amount of NaCl in the mixture = 1.169 gms.

(10) 0.109 gm. of a metal was dissolved in dilute sulphuric acid and the hydrogen produced was exploded with 25 c.c. of dry oxygen at N.T.P. The residual hydrogen gas at the same temperature and pressure occupies 25 c.c. Calculate the equivalent weight of the metal.

25 c.c. of oxygen combine with 50 c.c. of hydrogen

\therefore Total vol. of hydrogen liberated by the metal = $50 + 25 = 75$ c.c.

At N.T.P. gm - atomic vol. of hydrogen = 11.2 litres
 $= 11200$ c.c.

(\therefore hydrogen molecule is diatomic)

$$\therefore 75 \text{ c.c. of hydrogen} = \frac{75}{11200} \text{ mole equivalent of hydrogen}$$

Let the eq wt of the metal be x , then

$$0.109 \text{ gm of the metal} = \frac{0.109}{x} \text{ mole equivalent of the metal}$$

\therefore According to the definition,

$$\frac{75}{11200} = \frac{0.109}{x} \quad \text{or } x = \frac{0.109 \times 11200}{75} = 16.27$$

(11) 0.3975 gm of copper oxide was heated in a current of dry, pure hydrogen and 0.3175 gm of copper was obtained. Calculate the equivalent weight of copper.

Wt of copper oxide - wt of oxygen = wt of copper

$$\therefore \text{wt of combined oxygen} = 0.3975 - 0.3175 = 0.0800 \text{ gm}$$

8 gms of oxygen = 0.25 mole of oxygen and

$$0.08 \text{ gm of } \text{O}_2 = \frac{0.08}{32} \text{ mole of oxygen.}$$

Now, $\frac{0.08}{32}$ mole of oxygen combines with 0.3175 gm of copper

$$\therefore 0.25 \text{ " " " " " " } \frac{32 \times 0.3175 \times 0.25}{0.08} \text{ or } 31.75 \text{ gms of copper}$$

$$\therefore \text{Eq. wt of copper} = 31.75$$

Alternatively, mole equivalent of oxygen = 8. Let the equivalent weight of copper be x

$$\therefore \frac{\text{mole equivalent of oxygen}}{\text{eq. wt of copper}} = \frac{0.080 \text{ gm}}{0.3175 \text{ gm}}$$

$$\text{or, } \frac{8}{\text{eq. wt of copper}} = \frac{0.080}{0.3175} \quad \text{or } x = 31.75$$

(12) A solution containing 0.75 gm of zinc chloride when treated with excess of silver nitrate solution gave 1.5825 gms of silver chloride. What is the equivalent weight of zinc? ($\text{Ag} = 107.88$, $\text{Cl} = 35.46$)

Mole equivalent of silver chloride

$$= 107.88 + 35.46 = 143.34 \text{ gms.}$$

$$1.5825 \text{ gms of silver chloride} = \frac{1.5825}{143.34} \text{ mole equivalent of AgCl}$$

Let the mole equivalent of ZnCl_2 be x ; then 0.75 gm of zinc chloride = $\frac{0.75}{x}$ mole equivalent of ZnCl_2

$$\therefore \frac{0.75}{x} = \frac{1.5825}{143.34}$$

$$\therefore x = 67.93 \text{ gms. } \therefore \text{Eq. wt of } \text{ZnCl}_2 = 67.93$$

$$\text{Eq. wt of zinc} = \text{Eq. wt of zinc chloride} - \text{Eq. wt. of chlorine} = 67.93 - 35.46 = 32.47$$

CHAPTER 6

ACIDS, BASES AND SALTS

Acids : Ordinarily, an acid is a compound the molecule of which contains one or more hydrogen atoms replaceable partially or completely, directly or indirectly by a metal or a group of elements behaving like a metal to produce salt.

Certain metals which are much more electropositive than hydrogen (viz. metals which are placed above hydrogen in the electro-chemical series*) react with many acids and liberate hydrogen gas. In these cases, the displacement of hydrogen of the acids takes place directly. But in majority of cases, this displacement process occurs through reactions between the acids and the oxides or hydroxides of metals.

Hydroxides are the compounds containing an atom of a metal (or a metal like radical**) united with one or more hydroxy (OH) groups. The product formed by the partial or total replacement of hydrogen atom or atoms present in the molecule of an acid by a metal or a group of elements acting like a metal is known as a salt.

There are certain properties which are common to almost all acids. Generally, the aqueous solutions of acids have a sour taste. Most acids turn blue litmus red and react with metallic oxides or hydroxides (bases) with the formation of salts and water.

Acids are also characterised by their tendency to react with metal carbonates and bicarbonates evolving carbon dioxide. In aqueous solutions, the acids conduct electricity.

metal	acid	salt	metallic oxide	acid	salt	water
Zn	+ H ₂ SO ₄	= ZnSO ₄ + H ₂	MgO	+ H ₂ SO ₄	= MgSO ₄	+ H ₂ O
Mg	+ 2HCl	= MgCl ₂ + H ₂	CaO	+ 2HNO ₃	= Ca(NO ₃) ₂	+ H ₂ O
Hydroxide	acid	salt	water			
KOH	+ HNO ₃	= KNO ₃ + H ₂ O	Na ₂ CO ₃	+ H ₂ SO ₄	= Na ₂ SO ₄	+ CO ₂ + H ₂ O
Ca(OH) ₂	+ 2HCl	= CaCl ₂ + 2H ₂ O	NaHCO ₃	+ HCl	= NaCl + CO ₂	+ H ₂ O

So, the above hydrogen containing compounds like HCl, HNO₃, H₂SO₄ are acids.

* The electro-chemical series of metals has been discussed in chapter 7 of this book.

** Ammonium radical consisting of one atom of nitrogen and four atoms of hydrogen i.e. NH₄ is a familiar metal-like radical.

It is to be noted that any acid contains hydrogen but any compound containing hydrogen is not an acid. A compound containing one or more than one hydrogen atom in its molecule will be termed as an acid only when its hydrogen atom or atoms are replaceable by a metal and the product thus obtained must be a salt. None of the four hydrogen atoms of methane (CH_4) can be replaced by a metal. The metals like sodium, potassium displace hydrogen from water (H_2O), but the product obtained in each is not a salt. So, methane and water, though they contain hydrogen atoms in their molecules are not acids.

Classification of acids: Acids are generally divided into two classes: (a) Hydracids and (b) Oxy-acids.

(a) *Hydracids:* The acids which contain hydrogen and a non-metallic element (other than oxygen) or a radical are known as hydracids. It is to be noted that the names of the hydracids usually begin with the prefix hydro and end with the suffix ic. For example,

HCl (hydrochloric acid)

HCN (hydrocyanic acid)

HI (hydroiodic acid)

H_2S (hydrosulphuric acid)

(b) *Oxy-acids:* The acids which contain oxygen besides hydrogen and a non-metallic element or a radical are called oxy-acids. In other words, acids containing oxygen are said to be oxy-acids. The oxy-acids are named according to the non-metallic elements present in them and their oxygen content. It is customary that the names of the acids having larger proportions of oxygen terminate in *-ic* and the names of the acids containing smaller proportions of oxygen end in *-ous*.

If an element forms a series of oxy-acids, the prefixes 'hypo' and 'per' are added to the names of the acids containing less oxygen than the *-ous* acid and more oxygen than the *-ic* acid respectively.

Acid producing element	Oxy-acids			
	-ic acid	-ous acid	hypo acid	per acid
Sulphur	H_2SO_4 sulphuric	H_2SO_3 sulphurous	$\text{H}_2\text{S}_2\text{O}_4$ hypo sulphurous	$\text{H}_2\text{S}_2\text{O}_8$ per sulphuric
Nitrogen	HNO_3 nitric	HNO_2 nitrous	$\text{H}_2\text{N}_2\text{O}_4$ hypo nitrous	
Chlorine	HClO_4 chloric	HClO_3 chlorous	HOCl hypo chlorous	HClO_4 per chloric
Phosphorus	H_3PO_4 phosphoric	H_3PO_3 phosphorous	H_3PO_2 hypophosphorous	

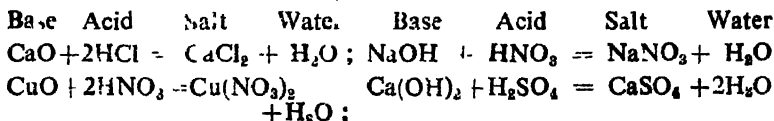
Acids may also be classified into (i) mineral acids and (ii) organic acids. The acids which can be derived from the mineral substances are known as mineral acids. Hydrochloric acid (obtained from common salt— NaCl), nitric acid (obtained from sodium or potassium nitrate), sulphuric acid (from sulphur), phosphoric acid (obtained from calcium phosphate) etc. belong to the class of mineral acids. The

acids which contain carbon as an essential element and can be obtained from either plants or animals are designated as organic acids. Formic acid (HCOOH), acetic acid (CH_3COOH) etc. are some of the well known organic acids.

A different way of classification is based on the number of replaceable hydrogen atom or atoms the acids contain. Thus, an acid is said to be *monobasic acid* if a molecule of it contains only one replaceable hydrogen atom e.g. HCl , HNO_3 , HClO_3 etc. Acetic acid (CH_3COOH), though containing four hydrogen atoms per molecule, is only monobasic as only one hydrogen atom of it can be replaced by a metal or a group of elements equivalent to a metal. Similarly, acids having two replaceable hydrogen atoms in each molecule are called *dibasic acids* and acids which contain three replaceable hydrogen atoms are called *tribasic acids*. H_2SO_4 , H_2SO_3 , H_2CO_3 etc. are the familiar examples of dibasic acids. H_3PO_4 is a tribasic acid. In general, acids having more than one replaceable hydrogen atom are termed as *polybasic acids*.

Bases : Bases belong to a class chemically opposite to the acids. Bases are usually the oxides or hydroxides of metals and react with acids to produce salts and water. The process in which an acid and a base react together in proper proportions and lose their individual characteristics with the formation of salt and water is known as *neutralisation*.

A base, if soluble in water, turns blue litmus red



Ammonia (NH_3) is not an oxide or a hydroxide of a metal but reacts with an acid to form a salt.

$\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$ (ammonium salt) Ammonia is regarded as a base although it does not conform to the above definition.

The nature of the hydroxides of the metals varies according to the position of the metal in the electrochemical series, as illustrated below.

<div> <div>K</div> <div>Na</div> <div>Ca</div> </div>	<div> <div>The hydroxides of the metals</div> <div>are soluble in water and</div> <div>are alkalis.</div> </div>	<div> <div>The hydroxides of sodium</div> <div>and potassium are not</div> <div>decomposed by heat.</div> </div>
<div> <div>Mg</div> <div>Al</div> <div>Zn</div> <div>Fe</div> <div>Pb</div> </div>	<div> <div>The hydroxides of the metals</div> <div>are insoluble in water. The</div> <div>hydroxides of magnesium</div> <div>and iron react with acids</div> <div>only but the hydroxides of</div> <div>aluminium, zinc and lead</div> <div>react with both acids and</div> <div>alkalis.</div> </div>	<div> <div>When heated, these</div> <div>hydroxides decompose into</div> <div>oxides of the metals and</div> <div>water.</div> </div>

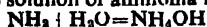
$\left. \begin{array}{l} \text{Hg} \\ \text{Ag} \\ \text{Au} \end{array} \right\}$ Hydroxides of these metals
do not exist.

Alkalis : Water-soluble hydroxides of metals are called alkalis.

The most common alkalis are sodium hydroxide (caustic soda) NaOH , potassium hydroxide (caustic potash) KOH , calcium hydroxide (slaked lime) Ca(OH)_2 . The alkalis possess the following characteristic properties.

(i) They react vigorously with acids to produce salts and water. (ii) Their aqueous solutions turn red litmus blue, phenolphthalein pink and methyl orange yellow. (iii) The aqueous solutions of alkalis are soapy to touch and conduct electricity.

N.B. (1) Ferric hydroxide Fe(OH)_3 , Zinc hydroxide Zn(OH)_2 , aluminium hydroxide Al(OH)_3 are water-insoluble hydroxides. They are bases but not alkalis. Thus, all alkalis are bases but all bases are not alkalis. (2) Ammonia (NH_3) dissolves in water producing ammonium hydroxide (NH_4OH) which shows alkaline properties. So, aqueous solution of ammonia is considered to be an alkali.



Basicity of an acid and acidity of a base : We know that an acid and a base in definite proportions neutralise each other to form salt and water. *The basicity of an acid is its power of neutralising a base and is expressed by the number of replaceable hydrogen atom or atoms the molecule of the acid contains.* For example,

Acid	Basicity
$\text{HCl}, \text{HBr}, \text{HNO}_3$	1 (monobasic)
$\text{H}_2\text{SO}_4, \text{H}_2\text{CO}_3, \text{H}_2\text{S}$	2 (dibasic)
H_3PO_4	3 (tribasic)

Acidity of a base is its power of neutralising an acid and is expressed by the number of replaceable hydroxyl groups present in each molecule of the base. For example,

Base	Acidity
NaOH, KOH	1 (monoacidic base)
$\text{Ca(OH)}_2, \text{Zn(OH)}_2, \text{Mg(OH)}_2$	2 (diacidic base)
Al(OH)_3	3 (triacidic base)

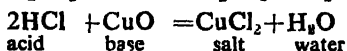
The acidity of a base which does not contain a (OH) group is measured by the number of molecules of a monobasic acid required to just neutralise one molecule of it. Thus CaO and Na_2CO_3 are diacidic bases as one molecule of each of the compounds requires two molecules of a monobasic acid (say HCl) for neutralisation.

Salts and their classification :

Salts : Salts are a class of compounds obtained by the partial or total replacement of the replaceable hydrogen atom or atoms present in the molecule of an acid by a metal or a group of elements behaving like a metal.

Acid	No of replaceable H-atom or atoms	Salt	
		H—partially displaced by a metal or group	H—totally displaced by a metal or group
HCl	1	—	NaCl, NH ₄ Cl
H ₂ SO ₄	2	NaHSO ₄ , NH ₄ HSO ₄	Na ₂ SO ₄ , (NH ₄) ₂ SO ₄

Salts may also be looked upon as the products formed in addition to water during neutralisation of acids by bases and vice versa.



Salts are generally grouped into three classes :

(A) **Normal salts** : The salts produced by complete displacement of all the replaceable hydrogen atom or atoms present in the molecule of an acid by a metal or a group equivalent to a metal are known as normal salts.

Examples :

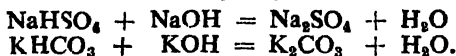
Acid	Normal salt
HCl	KCl, NH ₄ Cl
H ₂ SO ₄	K ₂ SO ₄ , (NH ₄) ₂ SO ₄
H ₃ PO ₄	K ₃ PO ₄ , (NH ₄) ₃ PO ₄

(B) **Acid salts or bi-salts** : The salts produced by the partial displacement of the replaceable hydrogen atoms present in the molecule of an acid by a metal or radical acting like a metal are called acid-salts or bi-salts.

Examples :

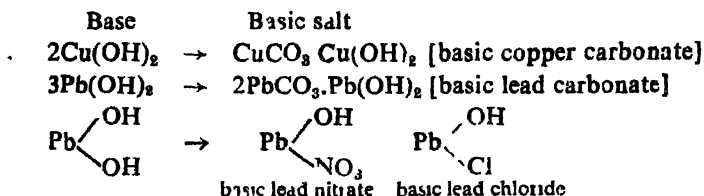
Acid	Acid or bi-salt
H ₂ SO ₄	NaHSO ₄ (sodium hydrogen sulphate or sodium bisulphate), NH ₄ HSO ₄ , Ca(HSO ₄) ₂ etc.
H ₂ CO ₃	NaHCO ₃ (Sodium bi-carbonate), NH ₄ HCO ₃ , Ca(HCO ₃) ₂ etc.
H ₃ PO ₄	NaH ₂ PO ₄ (mono sodium dihydrogen phosphate) Na ₂ HPO ₄ (di-sodium hydrogen phosphate)

Acid salts react with alkalis giving normal salts.

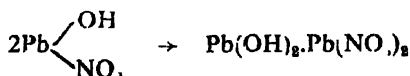


Soluble acid-salts like NaHSO₄, KHSO₄ generally give acid reaction to litmus. But NaHCO₃ is slightly alkaline in its reaction due to hydrolysis which will be discussed shortly.

(C) **Basic Salts** : The salts which are produced as a result of reaction of an acid with greater proportion of the base required to form a normal salt are called basic salts. A basic salt may also be taken as the product obtained by the partial replacement of the hydroxyl groups of a di or tri acidic base by an acid radical or a non-metal like Cl, NO₃, SO₄ etc.



A basic salt in many cases may be considered as the double compound of a normal salt and a base. For example,



Nomenclature of salts : In naming the salts, certain general rules are followed. A salt derived from a hydracid is named according to the non-metal present in the parent acid and the salt will end in -ide. Thus,

Acid	Salt
HCl	NaCl (Sodium chloride), MgCl ₂ (Magnesium chloride)
HBr	KBr (Potassium bromide), ZnBr ₂ (Zinc bromide)
HCN	NaCN (Sodium cyanide)
H ₂ S	K ₂ S (Potassium sulphide)

From the examples given above, it is clear that the metallic part of the salt is named first. The prefix hydro is dropped and the suffix -ic (of the acid) is changed to -ide.

A salt obtained from an oxy-acid is named according to the non-metal other than oxygen present in it and the suffix -ic of the acid is changed to -ate while -ous is changed to -ite. In other words, the -ic acids will produce -ate salts and the -ous acids will give -ite salts.

Acid	Salt
H ₂ SO ₄	Na ₂ SO ₄ (Sodium sulphate), CaSO ₄ (Calcium sulphate)
H ₂ SO ₃	K ₂ SO ₃ (Potassium sulphite)
HNO ₃	NH ₄ NO ₃ (Ammonium nitrate.)
HNO ₂	NH ₄ NO ₂ (Ammonium nitrite)

To name an acid salt, the word *bi-* or *hydrogen* is placed between the metallic and the acid parts while a basic salt is indicated by adding the word *basic* before the name of the salt. If the parent oxy-acid has any prefix such as *per*, *meta*, *hypo* etc. in its name, it will remain as such in the salt.

Acid	Salt
H_2SO_4	NaHSO_4 [sodium bi-sulphate or sodium hydrogen sulphate]
H_2CO_3	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ [basic copper carbonate]
$\text{H}_2\text{S}_2\text{O}_8$ (per sulphuric acid)	$(\text{NH}_4)_2\text{S}_2\text{O}_8$ [Ammonium per sulphate]
HPO_3 (meta phosphoric acid)	NaPO_3 [Sodium meta phosphate]
HOCl (hypochlorous acid)	KOC [Potassium hypochlorite]

Salts may have metals which can show variable valency. If the metal exhibits lower valency, the metallic part of the name ends in *-ous*, and if the metal shows higher valency, the same ends in *-ic*. Thus,

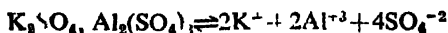
FeCl_2 (Ferrous chloride), FeCl_3 (Ferric chloride)

Double salts and complex salts : Salts so far described are said to be simple salts. In addition to them, there are two special types of salts known as the double salts and the complex salts.

Double salts : Sometimes, it so happens that when a solution of a normal salt is mixed with that of another normal salt in molecular proportions and the mixed solution is subjected to crystallisation, the crystals of a new, single salt separate out.

The salt thus obtained has definite number of water of crystallisation per molecule, definite crystalline structure and properties which are altogether different from those of the component salts. It contains both the normal salts in molecular proportions and exists as a stable compound only in the solid state. But in aqueous solution, it breaks up into its constituent salts which on dissociation give all the ions contained in the simple salts. Such a salt is called a double salt.

Potash alum having the molecular formula, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ is a familiar example of a double salt and is formed by the crystallisation of the solution containing K_2SO_4 and $\text{Al}_2(\text{SO}_4)_3$ in molecular proportions. It gives all the ions of its constituent salts when dissolved in water.



Complex Salts : Sometimes, the crystals of a new salt are formed when the solutions of two simple salts are mixed and the mixed solution is evaporated. The salt thus obtained is a distinct chemical substance in the solid state as well as in solution. In

aqueous solution, it does not dissociate into all the simple ions of the salts it is obtained from but yields complex ions along with the simple ions. Such a salt is known as a complex salt.

Potassium ferrocyanide $K_4Fe(CN)_6$, is a complex salt and is obtained on mixing the solution of ferrous sulphate with excess of potassium cyanide solution. From its composition $[Fe(CN)_6, 4KCN]$, it appears to be a mixture of ferrous cyanide and potassium cyanide in the ratio of 1 : 4. In aqueous solution, it never dissociates into K^+ , Fe^{2+} and CN^- ions but furnishes K^+ and the complex ferrocyanide ion, $[Fe(CN)_6]^{-4}$. Obviously, the solution of the salt will neither respond to the tests of ferrous ion nor those of the cyanide ion.



Ionisation of some complex salts is given below.



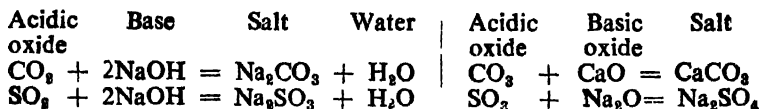
Cuprammonium sulphate



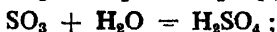
Potassium chloroplatinichloride

The oxides and their classification: The binary compounds which are formed by the chemical union of oxygen with other elements are known as oxides. Based on their characteristic properties, particularly their behaviour towards water and the nature of the compounds they form with it, oxides are classified into different groups.

(A) **Acidic oxides:** Generally, the non-metallic oxides which react with the bases to produce salts and water are called the acidic oxides. Carbon dioxide, sulphur dioxide, sulphur trioxide, nitrogen pentoxide etc. are acidic oxides. Sometimes, the acidic oxides combine with some metallic oxides having basic characters and yield salts.



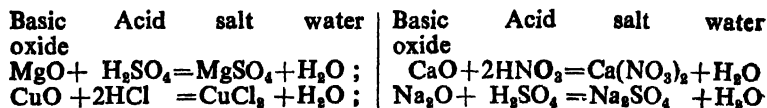
A soluble acidic oxide combines with water to form an acid that turns blue litmus red. In other words, an acidic oxide when soluble in water furnishes H^+ ions in solution.



The acidic oxide from which the acid is derived on treatment with water is often called the anhydride of the acid (acid anhydride means acid without water). Thus CO_2 and SO_2 are the anhydrides of carbonic and sulphurous acids respectively. Ordinarily, the acidic oxides do not react with mineral acids.

It is to be noted that higher oxides of some metals such as CrO_3 , Mn_2O_7 are acidic.

(B) Basic oxides: A basic oxide is a metallic oxide which reacts with acids to produce salts and water only. Thus, copper oxide, magnesium oxide, calcium oxide, sodium oxide etc. are basic oxides.



If soluble in water, a basic oxide forms a soluble base (alkali), which yields $-\text{OH}$ ions in solution and turns red litmus blue.

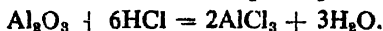
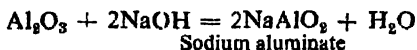
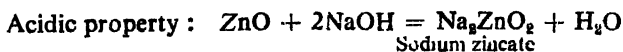


The oxides of the most active metals such as sodium, potassium, calcium etc. readily react with water giving the corresponding soluble hydroxides or alkalis but majority of the metallic oxides are insoluble and do not undergo any reaction with water. MgO is slightly soluble in water whereas CuO is insoluble.

An acidic oxide and a basic oxide are opposite to each other in respect of chemical characters and generally react with each other to give a salt. For example,



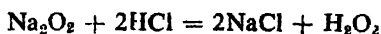
(C) Amphoteric oxides: The oxides which possess the properties of both acidic and basic oxides are known as amphoteric oxides. They can react with strong acids as well as with strong bases to produce salts and water. Usually, they are the oxides of metals of less electropositive character. Examples of this class are zinc oxide, aluminium oxide etc.



(D) Neutral oxides: The non-metallic oxides which show neither basic nor acidic characters i.e. which are indifferent towards acids or alkalis are called neutral oxides. If soluble in water, they do not change the colour of the litmus. Examples of such oxides are water, carbon monoxide, nitrous oxide (N_2O), nitric oxide etc.

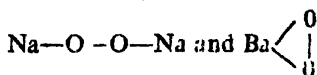
(E) Peroxides: A peroxide of an element is the oxide which contains the higher proportion of oxygen than what is present in its highest typical oxide (basic or acidic). For instance, the typical oxide of hydrogen is water (H_2O). Hydrogen forms another oxide containing more oxygen than that present in water. The second oxide is known as hydrogen peroxide (H_2O_2). Sodium peroxide

(Na_2O_2) and barium peroxide (BaO_2) are examples of peroxides in the sense of the above definition (The typical basic oxide of sodium is Na_2O and that of barium BaO). Peroxides of metals on treatment with cold dilute mineral acids produce hydrogen peroxide as one of the products.



When heated, a peroxide loses a part of its oxygen.

In peroxides, the oxygen atoms are linked not only to the atoms of the other element but also to themselves forming the oxygen chain, $-\text{O}-\text{O}-$ (commonly known as peroxy group). Thus, sodium peroxide and barium peroxide may be represented by the structural formulae given below :

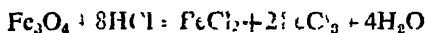


Based on the above discussions, a peroxide may be defined as an oxide whose oxygen content exceeds that of the typical oxide and which contains peroxy group readily hydrolysible to hydrogen peroxide with cold, dilute acids.

N.B. Oxides containing higher proportion of oxygen than the typical oxides are not always peroxide. For example, lead dioxide, PbO_2 (usual basic oxide of lead is lead monoxide - PbO), manganese dioxide MnO_2 (typical basic oxide of manganese is manganous oxide - MnO) do not yield hydrogen peroxide with dilute mineral acids and are not peroxides, in spite of their higher oxygen content.

(F) Mixed Oxides : A mixed oxide may be regarded as composed of two simpler oxides of the same element in different valency states. On treating with acids, such an oxide gives two different salts in which the other constituent element exhibits different valencies

Thus, ferrous ferric oxide having the molecular formula Fe_3O_4 appears to be a compound formed by ferrous oxide and ferric oxide (FeO , Fe_2O_3). It reacts with conc. hydrochloric acid to produce ferrous and ferric chlorides.



Red lead, Pb_3O_4 is another mixed oxide which may be represented as $\text{PbO}_2 \cdot 2\text{PbO}$.

Classification of oxides is shown in the following table.

Oxides					
Acidic	Basic	Amphoteric	Neutral	Per	Mixed

Acid, base and salt in the light of Arrhenius theory of electrolytic dissociation : In order to explain some of the characteristics of the electrolytes e.g. acids, bases or salts, Arrhenius put forward the

theory of electrolytic dissociation. According to this theory, a portion of the acids, bases or salts in the fused state or in aqueous solution splits up or dissociates spontaneously into positively charged and negatively charged smaller particles. The charged particles i.e. atoms or radicals thus produced as a result of electrolytic dissociation are called ions and the process of forming ions from an electrolyte either by dissolving in water or by fusion is called ionisation. The positively charged particles are known as positive ions or cations, while the negatively charged particles are negative ions or anions. The number of charges carried by an ion (cation or anion) is equal to its normal valency. The positive and negative charges are indicated by + and - signs respectively. The plus (+) sign represents unit of positive charge while the minus (-) sign denotes the unit of negative charge. Arrhenius theory further states that the ions formed in solution constantly reunite to form the neutral molecules and the ionised and non-ionised molecules remain in a state of equilibrium. Thus, the electrolytic dissociation is a reversible process.

	Cation	Anion
Acid—	$\text{HCl} \rightleftharpoons \text{H}^+$	$+ \text{Cl}^-$
Alkali—	$\text{Ca(OH)}_2 \rightleftharpoons \text{Ca}^{++}$	$+ 2\text{OH}^-$
Salt—	$\text{ZnCl}_2 \rightleftharpoons \text{Zn}^{++}$	$+ 2\text{Cl}^-$
Salt -	$\text{Al}_2(\text{SO}_4)_3 \rightleftharpoons 2\text{Al}^{++}$	$+ 3\text{SO}_4^{--}$

It is seen from the above examples that the number of positively charged cations and negatively charged anions may be same or different. But in all the cases, the total +ve charge carried by the cations is equal to the net -ve charge carried by the anions.

Discussions on acids, bases and salts in the light of electrolytic dissociation

Acids : An acid is a hydrogen-containing compound which when dissolved in water dissociates to produce hydrogen ions (H^+) as the only positive ions or cations. Examples are :

Acid	Cation	Anion	Acid	Cation	Anion
$\text{HCl} \rightleftharpoons \text{H}^+$	$+ \text{Cl}^-$		$\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{H}^+$	$+ \text{SO}_4^{--}$	
$\text{HNO}_3 \rightleftharpoons \text{H}^+$	$+ \text{NO}_3^-$		$\text{H}_2\text{CO}_3 \rightleftharpoons 2\text{H}^+$	$+ \text{CO}_3^{--}$	
$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+$		$(\text{CH}_3\text{COO})^-$ (acetate ion)	$\text{H}_3\text{PO}_4 \rightleftharpoons 3\text{H}^+$		PO_4^{--}

It may be mentioned here that a hydrogen ion in aqueous solution does not exist as the simple H^+ ion but it produces hydroxonium ion (H_3O^+) by uniting with each molecule of water.



But for ordinary purposes, the hydration of hydrogen ion is often ignored and H^+ is used. All characteristic properties of an acid are fully dependent on the hydrogen ions it produces. Thus

water-free pure hydrogen chloride (HCl) shows no acidity because it contains no H^+ ions.

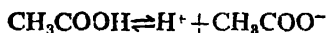
Again, the *basicity of an acid* is the number of hydrogen ion or ions which can be produced by one molecule of the acid.

Acid		Basicity
Hydrochloric	$HCl \rightleftharpoons H^+ + Cl^-$	1 (monobasic)
Nitric	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	1 („)
Acetic	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1 („)
Sulphuric	$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}$	2 (dibasic)
Carbonic	$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{--}$	2 („)
Phosphoric	$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{---}$	3 (tribasic)
Phosphorus	$H_3PO_3 \rightleftharpoons 2H^+ + HPO_3^{--}$	2 (dibasic)

It is clear from the table given above that basicity of an acid is not necessarily the number of hydrogen atoms present in one molecule of it. Acetic acid, having four hydrogen atoms in its single molecule is only mono-basic. Three of the four hydrogen atoms are so combined as to be incapable of ionising. Similarly phosphorus acid having three hydrogen atoms per molecule is dibasic. An acid is generally said to be polybasic when a molecule of it produces more than one H^+ ion in aqueous solution.

Strong and weak acids : The acids are divided into two classes depending on their tendencies to ionise.

The acids which are highly ionised in aqueous solutions giving large number of hydrogen ions are known as strong acids. HCl , HNO_3 , H_2SO_4 are examples of strong acids as the three acids, ionise almost completely in dilute solutions. On the other hand, the acids which in dilute solution produce small number of hydrogen ions are termed as *weak acids*. In other words, in the case of a weak acid, the ionisation is only slight and the major part remains as undissociated molecules. Acetic acid is a weak acid for it is about 0.4% ionised in water solution.



For thousand molecules 996 4 4

Carbonic acid (H_2CO_3) is also another familiar weak acid.

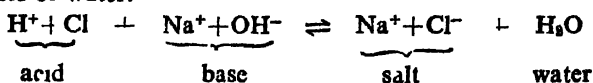
Bases : A base is a compound which when dissolved in water ionises to yield hydroxyl ions (OH^-) as the only negative ion or anion.

Base		Cation		Anion
$NaOH$	\rightleftharpoons	Na^+	+	OH^-
$Ca(OH)_2$	\rightleftharpoons	Ca^{+2}	+	$2OH^-$
NH_4OH	\rightleftharpoons	NH_4^+	+	OH^-

The characteristic properties of the aqueous solution of a base (alkali) are due to the OH^- ions released from it.

Again, a base may be defined as a substance which can combine with hydrogen ion H^+ (aq). During the formation of salt and water

by the interaction of an acid and an alkali, H^+ ions of the acid and OH^- ions of the base take the active part and produce undissociated molecules of water.



In short, we may say that an acid is a producer of H^+ while a base is that of OH^- in aqueous solution.

The *acidity of a base* is the number of hydroxyl ion or ions produced from one molecule of the base on ionisation. It may also be considered as the number of H^+ ions that can be accepted by one molecule of the base. Accordingly, the acidity of $NaOH$ is 1 i.e. it is mono acidic base. The acidity of $Ca(OH)_2$ is 2.

Strong and weak alkalis: The alkalis which are highly dissociated in aqueous solution to produce large amount of $(OH)^-$ ions are called *strong alkalis*. Examples are $NaOH$, KOH etc.

Again, an alkali is said to be weak when it is slightly ionised in water and the major part of it exists as undissociated molecules. Ammonium hydroxide (NH_4OH) is a weak alkali.

New ideas about acids and bases It is known that a 1H -hydrogen atom contains only one proton in its nucleus and just one electron outside the nucleus. If this single electron becomes detached the neutral hydrogen atom is evidently converted into a hydrogen ion (H^+) which is nothing but a bare hydrogen nucleus or a proton.



On the basis of the Brønsted and Lowry advanced the protonic concept for acids and bases. According to them, an acid is a substance which has the tendency to give up a proton i.e. acts as a proton donor and a base is a substance which has the tendency to take up a proton i.e. acts as a proton acceptor.

One of the significant results of this concept is that a neutral molecule as well as an ion can possess acidic or basic character in solution. Detailed discussions about the Proton Transfer Theory are not given as the student at the higher secondary level need not consider it.

Considering all the criteria, a more authoritative definition of an acid may be given as:

An acid is any compound which dissociates in water yielding hydrogen ions i.e. it is a substance which contains hydrogen atom in its composition which can either be a metal or a metal-like radical, reacts with certain metals to produce hydrogen, turns blue litmus solution red, and goes forward with bases to produce salts and salt water molecules, proton donor.

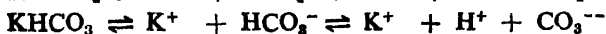
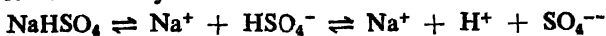
Salts: If a substance in aqueous solution can produce other positively and negatively charged ions in addition to H^+ and OH^- ions is a salt.

A normal salt is formed when all the H^+ of an acid is replaced by equivalent number of metallic or metal-like positive ions. In other words, a normal salt is a compound which dissociates in

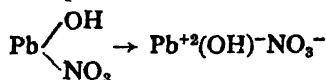
solution into positive ions (cation) other than H^+ ions and negative ions (anion) other than OH^- ions.

Normal Salt	Cation	Anion	Normal Salt	Cation	Anion
K_2SO_4	$\rightleftharpoons 2K^+$	$+ SO_4^{-2}$	$NaNO_3$	$\rightleftharpoons Na^+$	$+ NO_3^-$
$ZnCl_2$	$\rightleftharpoons Zn^{+2}$	$+ 2Cl^-$	Na_3PO_4	$\rightleftharpoons 3Na^+$	$+ PO_4^{-3}$

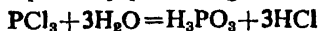
Acid salts or bi-salts ionise in solution into metallic ions (including NH_4^+) and negative ions, the latter being capable of further ionisation to yield H^+



* * Salts in which the OH^- ions together with positive metallic ions and negative ions are present are known as basic salts.



Hydrolysis: Hydrolysis may be regarded as a special type of double decomposition when a compound is split up by water either completely or partially producing new compounds. For example—



It is expected that the aqueous solutions of normal salts should always be exactly neutral in reaction. But in many cases solutions of such salts are found to exhibit either acidic or alkaline character to litmus. Thus, a solution of the normal salt sodium carbonate is alkaline and a solution of ammonium chloride acidic. This is due to the fact that when sodium carbonate is dissolved in water, a portion of the salt is decomposed by the solvent to produce sodium hydroxide (base) and carbonic acid. The solution is alkaline because $NaOH$ is a strong base and H_2CO_3 is a weak acid. Similarly ammonium chloride in aqueous solution reacts acidic as it partly decomposes to form hydrochloric acid (strong acid) and ammonium hydroxide (weak base).

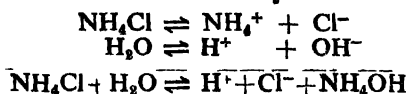
Such a process of decomposition of a neutral salt by water with the partial formation of the acid and the base from which the salt is obtained is known as hydrolysis of salts. The resulting salt solution reacts acidic or alkaline according to the acid or base being relatively strong. Hydrolysis of salts may be regarded as the partial reversal of neutralisation.

In the light of ionic theory or electrolytic dissociation, we can consider that this process occurs as a result of interaction between the ions produced from the salt and the ions produced from slightly ionisable water. The acidity or alkalinity of the solution of a salt

is due to the unequal ionisation of the acid and the base formed during hydrolysis.

Three types of salts mentioned below undergo hydrolysis.

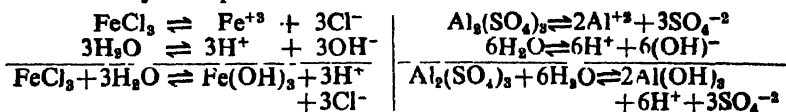
(A) *Salt of a strong acid and a weak base* : Ammonium chloride is a salt formed from the strong acid, hydrochloric acid and the weak base ammonium hydroxide. Its solution is acidic in reaction. When dissolved in water, the salt dissociates completely into NH_4^+ and Cl^- ions which interact with the ions (H^+ and OH^-) produced by the slight dissociation of water and yields highly ionisable HCl and almost undissociated ammonium hydroxide.



In this case, actually the cation of the weak base e.g. ammonium ion (NH_4^+) formed on dissociation of the salt reacts with water and withdraws OH^- ions produced from water with the formation of unionised NH_4OH . The solution reacts acidic as it contains excess of H^+ ions

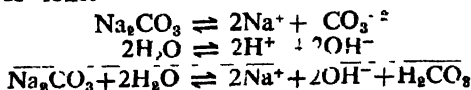


Acidity of the solution of ferric chloride or aluminium sulphate can similarly be explained.



$\text{Fe}(\text{OH})_3$ is a weak base while HCl is a strong acid which remains in solution as H^+ and Cl^- ions. $\text{Al}(\text{OH})_3$ is a weak base but H_2SO_4 ($2\text{H}^+ + \text{SO}_4^{-}$) is a strong acid.

(B) *Salt of a strong base and a weak acid* : Sodium carbonate is a salt produced by the reaction between a strong base (NaOH) and a weak acid (H_2CO_3). Its aqueous solution reacts alkaline. When dissolved in water, sodium carbonate ionises completely into Na^+ and CO_3^{-2} ions which react with the ions (H^+ and OH^-) produced from slight dissociation of water. As a result, sodium hydroxide and carbonic acid are formed in solution. Sodium hydroxide being a strong base remains as Na^+ and OH^- ions but the weak acid carbonic acid remains practically in the form of unionised molecules (H_2CO_3). The solution reacts alkaline as it has excess of OH^- ions.



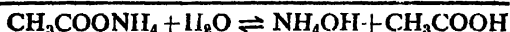
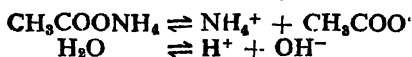
Actually, the anion of the weak acid i.e., CO_3^{-2} ions formed on dissociation of the salt react with H^+ ions produced from water forming undissociated weak acid (H_2CO_3) and leaving excess of OH^- ions in solution. So, the solution becomes alkaline.



Due to hydrolysis, the aqueous solution of potassium cyanide (KCN) which is a salt of a strong base (KOH) and a weak acid (HCN) reacts alkaline.

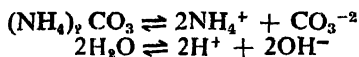
(C) *Salt of a weak acid and a weak base* : A salt of this type undergoes rapid hydrolysis producing the weak acid and the weak base from which the salt was obtained. The resulting solution in this case may be acidic, alkaline or even neutral depending upon the relative tendencies of ionisation of the acid and the base formed.

Hydrolysis of ammonium acetate :—



As both ammonia and acetic acid are equally weak, the solution of ammonium acetate in water inspite of hydrolysis remains neutral.

Hydrolysis of ammonium carbonate :



Ammonium carbonate hydrolyses in water to produce H_2CO_3 and NH_4OH , both of which are weak. But the solution reacts slightly alkaline, since ammonium hydroxide is stronger than carbonic acid.

Hydrolysis of ammonium formate :



The resulting solution is slightly acidic as ammonium hydroxide is weaker than formic acid.

N. B. (1) When a solution of sodium carbonate is added to a solution of aluminium chloride (or ferric chloride), the carbonate of aluminium (or iron) is never formed but its hydroxide is precipitated with the evolution of carbon dioxide. This is due to the fact that aluminium chloride (or ferric chloride) suffers hydrolysis producing hydroxide and free H^+ ions that decompose the carbonate into carbon dioxide.

(2) It is to be remembered that when a salt of a strong acid and a strong base such as sodium chloride is dissolved in water, the salt does not hydrolyse and the salt-solution is found neutral in reaction. Sodium chloride exists in aqueous solution as



If these two ions were to react with water, the products would be hydrochloric acid and sodium hydroxide. Both the products being strong electrolytes would dissociate into sodium ions and chloride ions and the hydrogen and the hydroxyl ions would recombine to produce water. Thus, there will not be any excess of H^+ or OH^- ions to give rise to acidity or alkalinity in the solution.

Equivalent weights of acids, bases and salts :

Equivalent weight and gram-equivalent of an acid : *The equivalent weight of an acid is the number of parts by weight of it which contains*

1 part (correctly 1.008 parts) by weight of replaceable hydrogen. Again, the basicity of an acid is the number of replaceable hydrogen atoms the molecule of the acid contains. So, the equivalent weight of an acid can be obtained from a simple relation stated below :

$$\text{Eq. wt. of an acid} = \frac{\text{Molecular weight of the acid}}{\text{Basicity of the acid}}$$

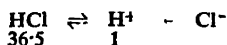
36.5 parts by weight of HCl contain 1 part (H=1.00) by weight of replaceable hydrogen e.g. the basicity of the acid is 1.

$$\therefore \text{Eq. wt. of HCl} = \frac{36.5}{1} = 36.5$$

Similarly, 98 parts by weight of H_2SO_4 contain 2 parts by weight of replaceable hydrogen i.e. basicity of the acid is 2.

$$\therefore \text{Eq. wt. of sulphuric acid} = \frac{98}{2} = 49$$

According to the ionic theory the equivalent weight of an acid is defined as the weight of the acid that gives 1.00 part by weight of hydrogen ion (H^+) in aqueous solution.



36.5 parts by weight of hydrochloric acid produce 1 part by weight of H^+ . Therefore, 36.5 is the equivalent weight of hydrochloric acid.

Equivalent weight (of the acid) when expressed in grams is called the gram-equivalent weight or simply gram-equivalent. Thus, *a gram-equivalent of an acid is that weight of it which contains 1.00 gram of replaceable hydrogen.* The gram-equivalent of an acid equals its gram-molecule divided by its basicity. Thus

$$\text{Gram-equivalent of nitric acid} = \frac{(1 + 14 + 48) \text{ gms}}{1} = 63 \text{ gms.}$$

Equivalent weights and gram-equivalents of some acids :

Acid	Molecular weight	Basicity	Eq. wt.	Gram-equivalent
Hydrochloric (HCl)	36.5	1	36.5	36.5 gms.
Nitric (HNO_3)	63	1	63	63 ..
Sulphuric (H_2SO_4)	98	2	49	49 ..
Phosphoric (H_3PO_4)	98	3	32.67	32.67 ..
Acetic (CH_3COOH)	60	1	60	60 ..
Oxalic ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)	126	2	63	63 ..

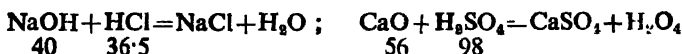
Equivalent weight and gram-equivalent of a base : *The equivalent weight of a base is the number of parts by weight of it which neutralises completely one equivalent of an acid.* Again, the acidity of a base (alkali) is the number of equivalents of an acid which can just be neutralised by one molecule of the base. In other words, the acidity of a base is the number of replaceable hydroxyl groups contained in its single molecule. So, the equivalent weight of a base may simply be expressed as

$$\text{Eq. wt. of a base} = \frac{\text{Molecular weight of the base}}{\text{Acidity of the base}}$$

Equivalent weight of a base expressed in grams is known as its gram-equivalent or gram-mole.

$$\therefore \text{Gram-equivalent of a base} = \frac{\text{Gram-molecular wt. of the base}}{\text{Acidity of the base}}$$

Example :



40 parts by weight of sodium hydroxide neutralise 36.5 parts by weight (or one equivalent) of HCl.

Therefore, acidity of NaOH is 1.

$$\therefore \text{Eq. wt. of NaOH} = \frac{23+1}{1} = 24 \text{ and its gram-equivalent is } 40 \text{ gms.}$$

Similarly, 56 parts by weight of CaO completely neutralise 98 parts by weight (or two equivalents) of H_2SO_4 . Therefore, acidity of CaO is 2. $\therefore \text{Eq. wt. of CaO} = \frac{56}{2} = 28$ and its gram-equivalent is 28 gms.

The equivalent weight of an alkali may also be defined as the weight of it which contains 17 parts by weight of replaceable hydroxyl group and can simply be expressed as

$$\begin{aligned} \text{Eq. wt. of an alkali} &= \frac{\text{Mol. wt. of the alkali}}{\text{Acidity of the alkali}} \\ &= \frac{\text{Mol. wt. of the base}}{\text{Number of (OH) groups present in the alkali}} \end{aligned}$$

$$\therefore \text{Eq. wt. of Ca(OH)}_2 = \frac{40+2 \times 17}{2} = \frac{74}{2} = 37.$$

Equivalent weights and gram equivalents of some alkalis :

Alkali	Mol wt	Acidity	Eq. wt	gm equivalent
Caustic soda NaOH	40	1	40	40 gms.
Caustic potash, KOH	56	1	56	56 „
Calcium hydroxide, Ca(OH)_2	74	2	37	37 „
Ammonium hydroxide NH_4OH	35	1	35	35 „

In case of a basic oxide, the equivalent of it may be expressed as follows

$$\text{Eq wt of a basic oxide} = \frac{\text{Mol wt of the oxide}}{\text{Number of atoms of the metal} \times \text{valency of the metal}}$$

Equivalent weight and gram equivalent of a salt (Normal) :

The equivalent weight of a salt is the part by weight of it which contains one equivalent of the constituent metal or the radical equivalent to a metal

It can be known from the simple relation stated below.

$$\text{Eq. wt of a salt} = \frac{\text{Mol wt of the salt}}{\text{Total number of metal atoms} \times \text{valency of the metal}}$$

In sodium chloride, NaCl ($23 + 35.5$) or 58.5 parts by weight of the salt contain 23 parts by weight (one equivalent) of sodium. Hence, equivalent weight of $\text{NaCl} = 58.5$. Similarly, ($40 + 12 + 48$) or 100 parts by weight of calcium carbonate CaCO_3 contain 40 parts by weight or two equivalents of calcium. \therefore Eq wt. of calcium carbonate = $100 \div 2 = 50$. The equivalent weight if expressed in grams will give the gram equivalent of the salt.

Equivalent weight of some salts :

Salt	Mol wt	Number of metal atoms > valency	Eq. wt.
Sodium carbonate, Na_2CO_3	106	$2 > 1$	$106 - 2 = 53$
Aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$	342	2×3	$342 - 6 = 57$
Barium chloride, BaCl_2 , $2\text{H}_2\text{O}$	244	1×2	$244 - 2 = 122$
Copper sulphate, CuSO_4 , $5\text{H}_2\text{O}$	249.5	1×1	$249.5 - 2 = 124.75$
Silver nitrate, AgNO_3	170	1×1	170

The equivalent weight of a salt (such as a carbonate or a bi-carbonate) which reacts with an acid can be calculated as follows. The weight of the salt in grams, which neutralises one gm-equivalent of an acid is referred to as the gm-equivalent of the salt.



∴ Eq. wt. of Na_2CO_3 and NaHCO_3 are 53 and 84 respectively.

Solutions and their concentrations or strengths : The strength or concentration of a solution indicates the weight of a substance (solute) present in a given volume of the solution. It can be expressed in various ways. A solution which contains a known weight of the solute dissolved in a known volume of the solution is called a *standard solution*. Therefore, a standard solution is a solution of known strength or concentration.

Normal solution : The normal solution of a substance is that solution one litre (or 1000 ml) of which contains one gram-equivalent of the substance.

The gram-equivalents of HCl, NaOH are 36.5 gms. and 40 gms. respectively. So, the normal solution of hydrochloric acid contains 36.5 grams of HCl per litre of the solution. When 40 gms of NaOH are dissolved in one litre of distilled water, the resulting solution is a normal solution of caustic soda. A normal solution is indicated by 1N or (N) solution,

∴ One litre of (N) H_2SO_4 shall contain 49 gms of H_2SO_4

“ “ “ (N) KOH “ “ 56 “ “ KOH

“ “ “ (N) Na_2CO_3 “ “ 53 “ “ Na_2CO_3

“ “ “ (N) AgNO_3 “ “ 170 “ “ AgNO_3

Strength of solutions in terms of normality : *Normality of a solution denotes the number of gram-equivalents of a solute present in one litre of the solution. Thus—*

$$\text{Normality} = \frac{\text{Number of gm-equivalents of solute}}{\text{Number of litres of solvent (or solution)}}$$

The normality of a solution is 1 (or the solution is 1N) when it contains one gram-equivalent of the solute per litre. If one litre of a solution contains a quantity which is a multiple or a fraction of one gram-equivalent of the solute, the strength of such a solution in terms of normality is expressed in the following way.

Quantity of solute per litre	Name	Abbreviation	Normality of the solution
1 gm-equivalent	Normal	1N or N	1
3 gm-equivalents	Three normal	3N	3
$\frac{1}{2}$ gme-equivalent	Semi normal	$\frac{N}{2}$ or 0.5N	$\frac{1}{2}$ or 0.5
$\frac{1}{10}$ gm-equivalent	Deci normal	$\frac{1}{10}$ or 0.1N	$\frac{1}{10}$ or 0.1
$\frac{1}{100}$ gm-equivalent	Centi normal	$\frac{N}{100}$ or 0.01N	$\frac{1}{100}$ or 0.01

\therefore 1 litre of 3N H_2SO_4 solution will contain 49×3 or 147 gms of H_2SO_4 .

1 " " 2N Na_2CO_3 " " " " 53×2 or 106 gms of Na_2CO_3

" " " $\frac{N}{10}$ H_2SO_4 " " " " $49 \times \frac{1}{10}$ or 4.9 gms of H_2SO_4

" " " $\frac{N}{100}$ Na_2CO_3 " " " " $53 \times \frac{1}{100}$ or 0.53 gm of Na_2CO_3

" " " xN HCl " " " " $36.5 \times x$ or 36.5x gms of HCl

In volumetric analysis, normal and decinormal solutions are usually used.

Molar Solution : A molar solution of a substance is that solution one litre (or 1000 ml) of which contains one gram-molecular weight or gm-molecule (or 1 mole) of the substance.

One gram-molecular weight or one gm-molecule of H_2SO_4 is 98 gms.
" " " " " " " " " " of NaOH is 40 gms.

One litre of H_2SO_4 solution which contains 98 gms. of H_2SO_4 is called the molar solution of the acid. A molar solution of NaOH will contain 40 gms of NaOH per litre. A molar solution is represented by M.

Strength of solutions in terms of molarity : *Molarity of a solution is defined as the number of gm-molecules or simply moles of the solute present in one litre of the solution.*

The molarity of a solution is 1 or (the solution is 1 M) if it contains one gm-molecule of the solute per litre. A 2M solution of a substance shall contain two gm-molecules of the substance

in one litre. A 0.1M solution means a solution one litre of which contains one tenth of a gm-molecule of the solute.

$$\therefore \text{Molarity (M)} = \frac{\text{Number of gm-molecules of solute}}{\text{Number of litres of solvent (or solution)}}$$

N.B. It is clear that there is no difference between a molar and a normal solution of a substance the gm-molecule of which is identical with its gm-equivalent. Thus, the concentration of the solution of HCl, HNO₃, NaOH, or KOH is the same both in terms of normality and molarity. But the concentration of the molar solution of each of the substances like H₂SO₄, Na₂CO₃, Ca(OH)₂ will be twice the concentration expressed in the terms of normality.

Formal solution: With a view to expressing the strength of solutions of certain substances, it has now been preferred to use *formal concentration* or *formality* denoted by F.

A formal solution of a substance is that solution one litre of which contains one gram-formula weight (*i.e.* formula weight expressed in grams) of the substance and formality of a solution represents the number of gm-formula weights of a solute present in one litre of the solution.

$$\therefore \text{Formality} = \frac{\text{Number of gram-formula weights}}{\text{Vol. of solution in litres}}$$

A solution is said to be 1F or F when it contains one gm-formula weight of the solute per litre.

There are many strong electrolytes which actually do not exist in the molecular forms. They ionise completely in aqueous solution and remain as ions even in the solid state. Salts like NaCl, ZnCl₂, KNO₃ etc. belong to this class. A NaCl solution does not contain NaCl molecules but contains only Na⁺ and Cl⁻ ions. Again, in a solution of barium hydroxide [Ba(OH)₂·2H₂O], there is no molecule which corresponds to the formula Ba(OH)₂·2H₂O. Sodium carbonate (Na₂CO₃) when dissolved in water produces OH⁻ ions, due to hydrolysis. The solution-concentration of such substances is expressed logically in terms of formality. Its advantage over the molarity and normality is that it expresses the overall concentration of a solution without commitment as to the ionic or molecular species present.

One litre of (F) NaCl solution will contain 58.5 gms of NaCl

“ “ “ (F) Ba(OH)₂·2H₂O “ “ 207 “ “ Ba(OH)₂·2H₂O

A formal solution appears to be the same as the molar solution. But one should clearly understand the difference between the two. If the formula of a solute is the same as its correct molecular formula representing the molecules actually present in the solution, then formality and molarity become identical. Thus, 0.1F solution of glucose having the molecular formula C₆H₁₂O₆ is the 0.1M solution. But 0.1F solution of NaCl cannot be regarded as its 0.1M solution. It is preferably stated as 0.1M in Na⁺ ions and 0.1M in Cl⁻ ions.

Molar solution has not been included in the Higher Secondary Syllabus of West Bengal.

Molality and molal solution : Sometimes, the concentration of a solution is expressed in terms of molality which is the number of moles of the solute dissolved in 1000 gms of the solvent. A *molal solution* of a substance is that solution which contains one mole of the substance per 1000 gms of the solvent. The letter *m* is used to denote a solution which is one molal.

The strength of solution are also expressed by the following ways.

(A) **Percentage strength :** The percentage (%) strength of a solution is the number of grams of the solute present in 100 ml of the solution. Thus, a 5% NaOH solution means a solution 100 ml of which contain 5 gms of NaOH. In a 10% HNO₃ solution, 10 gms of HNO₃ are present in 100 ml of it.

(B) **Strength in terms of gms/litre :** The strength may also be denoted by the number of gms of the solute dissolved in one litre or 1000 ml of the solution. Thus, when one litre of NaOH solution contains 10 gms of the solute, the strength of the solution is said to be 10 gms/litre.

Conversion of one strength into another :

(A) **Per cent strength to normality :**

100 ml of 5% NaOH solution will contain 5 gms of NaOH

∴ 1000 ml „ „ „ „ „ „ 5 × 10 gms of NaOH.

By definition, a normal solution of NaOH is one which contains 40 gms. of it per litre of the solution.

Thus,

40 gms of NaOH present in 1000 ml give 1N NaOH

∴ 50 „ „ „ „ „ „ $\frac{5 \times 10}{40}$ N

or, 1.25 NaOH

When the percent strength of a solution is A, its strength in terms of normality $\frac{A \times 10}{\text{gm-equivalent of solute}}$

(B) **From normality to gms/litre :**

Amount of solute present per litre of 1N soln = 1 × gm-equivalent of solute (as per definition)

∴ „ „ „ „ „ 2N soln. = 2 × gm-equivalent of solute

„ „ „ „ „ $\frac{1}{10}$ N soln = $\frac{1}{10}$ × gm-equivalent of solute.

∴ Weight in gms/litre = Normality × gm-equivalent.

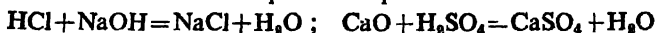
∴ Normality can be obtained on dividing the amount of solute in gms/litre by gm-equivalent of the solute.

Acidimetry and Alkalimetry :

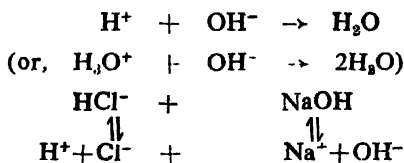
Neutralisation : Acids and bases are opposite in their chemical characteristics. As soon as an acid and a base come in contact with each other, they react to produce salt and water. When equivalent quantities of an acid and a base in aqueous solution are mixed the resulting solution usually becomes neutral due to the formation of neutral salt and water. Such a reaction is called neutralisation.

Generally, neutralisation means the complete combination of the replaceable hydrogen (H) present in an acid with the oxygen (O) or hydroxyl groups (OH) present in a base (basic oxide or hydroxide) forming neutral water and a salt.

Obviously, the acid and the base involved in the process of neutralisation must be in equivalent quantities.



According to the ionic theory, neutralisation is the process in which the hydrogen ions, H^+ (or hydroxonium ions, H_3O^+) of the acid and the hydroxyl ions, OH^- of the base interact to form undissociated molecules of water. A neutral salt is produced at the same time.



Indicators : In volumetric analysis, certain chemical substances are used, which essentially by change of their colours or otherwise indicate the end point or completion of a chemical reaction. Such substances are called indicators.

Various types of indicator are known.

The chemical substance which by change of its colour determines the end point of neutralisation or the moment of completion of a reaction between an acid and an alkali is known as the acid-base indicator, neutralisation indicator or hydrogen ion indicator.

An indicator of this type changes its colour according to whether the solution is acidic, alkaline or neutral. For example,

Litmus is an acid-base indicator. It is red in contact with an acid solution, blue in alkaline solution and purple or violet in a neutral solution. So, it can indicate the acidic, alkaline or neutral character of a solution to which it is added. Methyl orange and phenolphthalein are two acid-base indicators which are often used. Their colours in acidic, alkaline and neutral media are given here.

Indicator	Colour in acidic soln.	Colour in alk. soln.	Colour in neutral soln.
Methyl orange	Red or pink	Yellow	Orange
Phenolphthalein	Colourless	Pink	Colourless

It is to be noted that an indicator generally does not influence the progress of a reaction.

Selection of indicators: Use of indicators in studying the neutralisation reactions is practically indispensable and as such the selection of a suitable indicator to determine the correct end-point of a reaction is of primary importance. The choice of acid-base indicators depends on the strength of acids and bases taking part in neutralisation i.e. on the acid, alkaline or neutral character of the solution of the salt after neutralisation. We know that in a neutralisation process, equivalent amounts of an acid and a base react completely to produce salt and water. But the resulting solution of the salt thus formed may or may not be exactly neutral. On the other hand, the solution of the salt as a result of hydrolysis may be either slightly acidic or alkaline. Neutralisation involving a strong base and a weak acid (say CH_3COOH + NaOH) results in the formation of a salt which suffers hydrolysis giving a slightly alkaline solution at the end point. In such a case, phenolphthalein is the suitable indicator as it changes its colour in alkaline solution. For the similar reason, neutralisation of a strong acid by a weak alkali gives a slightly acidic solution at the end point. Here, methyl orange is a good indicator as it changes its colour in acidic solution. The salt formed as a result of neutralisation between a strong acid and a strong alkali does not undergo hydrolysis and hence its aqueous solution at the end point is exactly neutral. An indicator can be used in such a case.

Strength of acid and base involved in neutralisation	Indicator to be used
1. Strong acid—strong base e.g. $\text{NaOH} + \text{HCl}$	Any indicator
2. Strong acid—weak base e.g. $\text{H}_2\text{SO}_4 + \text{Na}_2\text{CO}_3$	Methyl orange
3. Weak acid—strong alkali e.g. $\text{CH}_3\text{COOH} + \text{NaOH}$	Phenolphthalein
4. Weak acid—weak base	No suitable indicator.

N.B. At this stage, it is not possible to discuss in detail the chemical nature of the indicators and the principles on which their selection is based. In selecting an indicator, the following points are to be taken into account.

(1) To determine the end point of a neutralisation reaction, litmus is not generally used. This indicator is not at all used in the acid-base reaction which liberates an acidic oxide (such as carbon dioxide) as one of the products. Methyl orange can be used in this case.

(2) If ammonia is evolved during the reaction between an acid and an alkali, phenolphthalein should not be used.

✓ (3) If phenolphthalein is used as an indicator during the neutralisation of sodium carbonate with a strong acid like HCl or H_2SO_4 , it becomes colourless (i.e. pink colour in Na_2CO_3 solution disappears) when only half of Na_2CO_3 is neutralised. This is due to the fact that the reaction between Na_2CO_3 and a strong acid takes place in two stages. In the first stage, Na_2CO_3 is converted into NaHCO_3 , alkalinity of which is not indicated by phenolphthalein. In other words, NaHCO_3 solution is not alkaline to phenolphthalein and as such it changes its colour from pink to colourless.



By using methyl orange, the end point of neutralisation of bicarbonate can be determined. It is found that the volume of the acid required to determine the end point of the first stage (using phenolphthalein as the indicator) is equal to the volume of the acid necessary to complete the neutralisation (using methyl orange).

Distinction between neutralisation and hydrolysis.

Neutralisation	Hydrolysis
1. Neutralisation is a reaction involving the union of H^+ ions of an acid and OH^- ions of an alkali to form undissociated water when both the acid and alkali are in equivalent amounts.	1. Hydrolysis is a special type of double decomposition in which water in addition to its function as a solvent splits up a neutral salt partially to form the acid and the base from which the salt is derived. In short hydrolysis is a partial reversal of hydrolysis.
2. In neutralisation, the acid and the base are the reactants while the salt and water are the products.	2. In hydrolysis, the salt and water are the reactants and the acid and the base are the products.
3. The process of neutralisation takes place irreversibly.	3. The hydrolysis is a reversible process.
4. Any acid and base can take part in neutralisation.	4. All salts do not undergo hydrolysis. For example, salts of strong acids and strong bases (NaCl , K_2SO_4 etc.) do not suffer hydrolysis.

Acidimetry : Acidimetry is a process by which the unknown strength of an acid solution (i.e. the quantity of an acid in a given volume) is determined by neutralising it with a solution of an alkali of known strength (i.e. a standard solution) in presence of an indicator.

Alkalimetry : Alkalimetry is the process by which the unknown strength of an alkali solution is determined by neutralising it with a solution of an acid of known strength in presence of a suitable indicator.

N. B. Definitions of acidimetry and alkalimetry, according to some chemists, are just the reverse of what are stated here.

The experimental procedure of determining the volume of a solution of unknown strength or concentration, which is just necessary to react completely with a definite volume of another standard solution is known as *titration*. The titration involving neutralisation of an acid by an alkali or vice versa is termed acid-base titration. In the process of titration, a stage or point is reached when the reaction is just complete. This point is called the *end point* and is usually determined by using an indicator.

Some fundamental principles of acidimetry and alkalimetry :

(A) We know that a normal solution of a substance contains one gm-equivalent of the substance dissolved in one litre of it. Hence, 5N solution and $\frac{1}{5}$ N solution will contain respectively 5 gm-equivalents and one tenth of one gm-equivalent of the solute per litre.

\therefore 1 ml of 5 (N) soln. \equiv 5 ml of (N) soln \equiv 50 ml of $\frac{1}{10}$ (N) soln.

and 1 ml of (N) soln. \equiv 10 ml of $\frac{1}{10}$ (N) soln. \equiv 2 ml of $\frac{N}{2}$ soln. \equiv

100 ml of $\frac{N}{100}$ soln.

Thus, y ml. of x (N) soln. $\equiv (y \times x)$ ml. of (N) soln.
 $\equiv x$ ml. of y (N) soln.

\therefore Volume of a given solution is inversely related to its strength.

(B) We know that in neutralisation acids and alkalis react with each other in equivalent amounts. 1 gm-equivalent of any acid will neutralise completely 1 gm-equivalent of any base. The neutralising power of 1 gm-equivalent of any acid is the same. This is equally true in the case of any alkali.

\therefore 49 gms of H_2SO_4	40 gms of NaOH
\equiv 40 " " NaOH	\equiv 36.5 gms of HCl
\equiv 56 " " KOH	\equiv 63 gms of HNO_3
\equiv 53 " " Na_2CO_3	\equiv 32.67 gms of H_3PO_4
\equiv 35 " " NH_4OH	

Again, 1000 ml. (N) acid \equiv 1000 ml. (N) alkali

2000 ml. " " \equiv 2000 " " "	
10 ml " " \equiv 10 " " "	
1 ml. " " \equiv 1 " " "	
V ml. " " \equiv V " " "	

∴ Solution of an acid and a base of the same strength in terms of normality must neutralise each other in equal volumes.

(C) If V_1 ml. of a S_1 (N) acid solution is neutralised by a S_2 (N) solution of an alkali, then the volume of the alkali required can be calculated easily.

V_1 ml. of S_1 (N) acid soln. $\equiv V_1 S_1$ ml. of (N) acid soln.

Let V_2 be the required vol. of alkali of the strength S_2 (N)

$\therefore V_2$ ml. of S_2 (N) alkali soln. $\equiv V_2 S_2$ ml. of (N) alkali soln.

As stated earlier, the solutions of an acid and a base of the same normality react in equal volumes.

$\therefore V_1 S_1 = V_2 S_2$ or Volume of the acid \times strength of the acid \equiv Volume of the alkali \times strength of the alkali.

This is the most important and fundamental equation in acidimetry and alkalimetry.

Alternatively, by definition, normality = gm-equivalents--weight in gms./litre.

\therefore Normality = $\frac{\text{Number of gm-equivalents of solute}}{\text{volumes in litres}}$

Or, Number of gm-equivalent = $N \times \text{vols. in litres}$

Now, solutions of two substances reacting with each other completely must contain the same number of gram-equivalents.

\therefore Normality of the solution I \times Number of litres = Normality of the solution II \times Number of litres.

When both the solutions are of known strength (vols. expressed in ml.), the product of the volume and strength of solution I equals the product of the volume and strength of solution II.

If V_1 and V_2 are the volumes of the two solutions and S_1 and S_2 are their strengths in normality, then

$$V_1 S_1 = V_2 S_2$$

(D) *Reduction of strength by dilution:* From all the foregoing discussions it is clear that the strength or concentration of a solution for a given weight of solute is inversely related to the volume of the solution.

or, $V \propto \frac{1}{S}$ (where S = strength and V = volume)

So, if the volume of the solution is increased i.e. the solution is diluted, its strength is proportionately reduced. Evidently a solution of higher strength may easily be converted to a solution of any desired but lower strength by dilution.

Let 25 ml. of (N) acid solution \equiv 10 ml. of an alkali solution of unknown strength. Obviously, the alkali solution is stronger than the acid. To reduce the strength of the alkali solution to exactly

carefully washed down into the flask with a jet of little distilled water so that no solid particle of sodium carbonate remains

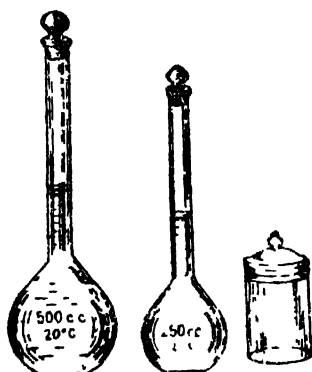


Fig. 1.25) Measuring flasks and weighing bottle

adhered to the flask or the stem of the funnel. Now adding a little more distilled water, the flask is shaken thoroughly till dissolution of the solid carbonate is complete. Then by gradual addition of water, the volume of the solution is made up to the mark on the neck of the flask indicating 250 ml. It is to be remembered that the lowest edge of the curved surface of the solution must touch the mark.

Now, the flask is closed with its stopper and shaken well to get a uniform solution.

The strength of the Na_2CO_3 solution prepared.

Let the amount of sodium carbonate actually taken = 1.3850 gms.

Now, 1.3250 gms of Na_2CO_3 , when present in 250 ml, the strength of the soln. is $\frac{N}{10}$

\therefore 1.3850 gms of Na_2CO_3 , when present in 250 ml, the strength of the soln. = $\frac{1.3850}{1.3250} \times \frac{N}{10}$

or, 1.0452 $\frac{N}{10}$.

N.B. It is not at all desirable to add water up to the mark at a time. Water is to be added, first in small quantities to dissolve the sodium carbonate taken. More water is then added to make the volume of the solution just 250 ml.

Factor: In most of the cases, it is extremely difficult or practically impossible to weigh the exact quantity of a substance (solute) required to prepare its solution of given strength. Usually, a quantity of the solute which is a little less or more than the required amount is taken.

Thus, in the preparation of 250 ml of $\frac{N}{10}$ Na_2CO_3 solution described above, 1.385 gms of Na_2CO_3 have been taken instead of the theoretical weight 1.325 gms. The solution thus obtained is a standard solution, the strength of which is $\frac{1.385}{1.325} \times \frac{N}{10}$ or 1.0452 $\left(\frac{N}{10}\right)$. Here,

1.0452 is the factor of $\frac{N}{10}$ Na_2CO_3 solution and the solution is a bit stronger than the exact $\frac{N}{10}$ solution. 4 gms of caustic soda per litre gives a $\frac{N}{10}$ solution. If we dissolve 3.9824 gms/litre, we get $\frac{N}{10}$ NaOH solution $(f = \frac{3.9824}{4.0030})$

Thus the factor is the ratio of the weight of the substance actually taken to the theoretical weight of it required to prepare a solution of given strength.

or, factor

$$\frac{\text{weight of the substance actually dissolved}}{\text{weight required to be dissolved to make a solution of given strength}}$$

(b) To prepare a litre of approximately $\frac{N}{10}$ solution of sulphuric acid. The gm equivalent of sulphuric acid is 49 gms. To prepare one litre of $\frac{N}{10}$ solution H_2SO_4 required is 49 gms.

Sulphuric acid is a highly hygroscopic liquid and is not obtained in the pure form. Generally the available acid contains 96 to 98 percent of the pure acid (by weight). So it is not possible to weigh out 49 gms of the acid correctly with the help of a chemical balance. In this case from the specific gravity and the purity of the acid supplied, the volume of the concentrated acid that contains 49 gms of the acid is first calculated.

Let the purity of the acid supplied be 97 percent.

i.e., 97 gms of pure acid are present in 100 gms of the conc. acid.

$$49 \text{ , , , , , } \frac{100 \times 49}{97}$$

or 50.51 gms of the conc. acid

Let the density of 97% H_2SO_4 be 1.84

$$\text{Now } D (\text{density}) = \frac{M (\text{mass})}{V (\text{volume})} \therefore V = \frac{M}{D} = \frac{50.51}{1.84} = 27.4 \text{ ml.}$$

27.4 ml of conc. acid will contain 49 gms of the pure acid. Now 28 ml of conc. sulphuric acid are measured out by a measuring cylinder and poured carefully with shaking into a litre flask containing about 500 ml of distilled water. The solution is cooled and diluted with water upto 1000 ml mark. The solution thus prepared is approximately $\frac{N}{10}$.

Similar procedure is applied for preparing approximately standard solutions of HCl and HNO_3 .

The volume of acid to be taken in preparing one litre of approximately $\frac{N}{10}$ H_2SO_4 solution can also be calculated thus—

The concentrated sulphuric acid generally used in the laboratory is 36N.

Let the vol. of the acid required be x ml,

then $x \times 36N = 1000 \times \frac{N}{10} \therefore x = 28 \text{ ml (nearly)}$

There are some chemical substances which are readily available in pure and dry form. The standard solution of such a substance can be prepared by dissolving a known weight of it in definite volume of water. The strength of this solution is directly known and remains unchanged for a considerable period of time. The standard solution thus prepared is known as a *primary standard solution* and the substances used for making primary standard solutions are called *primary standards*. Substances, like anhydrous sodium carbonate, oxalic acid crystals etc. are commonly used as primary standards.

On the other hand, there are substances which are not readily available in sufficiently pure and anhydrous state and cannot be accurately weighed out. A solution obtained by dissolving a certain weight of such a substance cannot be regarded as a solution of known strength. In this case, an approximate weight of the substance is dissolved in almost definite volume of water so as to give a solution of approximate strength. The solution thus prepared is subsequently titrated with another primary standard solution to determine its actual strength. Such a standardised solution used in volumetric analysis is known as a *secondary standard solution* and the substances used to prepare secondary standard solutions are called secondary standards. Sodium hydroxide, potassium hydroxide, sulphuric acid, nitric acid etc. are all secondary standards.

Determination of the strength of a solution by titration. The strength of a solution of unknown strength can be determined by titration against a standard solution of another suitable substance. The details of the apparatus (such as pipette, burette, wash-bottle, measuring flasks etc.) which are commonly used in volumetric analysis can be known from any book on analytical chemistry.

Determination of exact strength of an approximately $\frac{N}{10}$ H_2SO_4 solution by titration with a standard solution of Na_2CO_3

Procedure. A clean 50 ml burette is washed thoroughly at least twice with distilled water. The burette is then rinsed with a few ml of the acid the strength of which is to be determined. Now, the burette is filled up 1 cm or so above the zero mark with the given acid and the acid is run through the tap till the lowest edge of the meniscus touches the zero mark. Care must be taken so that no air bubble is left in the liquid inside the burette. It is then clamped to a stand vertically.

A 25 ml. pipette is washed first with distilled water and then rinsed with a few ml of the given alkali solution. 25 ml of the standard solution of sodium carbonate is then taken by means of the pipette in a clean beaker. To transfer the last drop, the tip of the pipette is touched inside surface of the beaker. (The last drop is never blown out.)

The solution is diluted to about 50 ml with distilled water and two drops of methyl orange solution (indicator) are added to this solution when it turns yellow. The acid solution from the burette is then gradually added dropwise to the alkali solution with constant stirring with a glass rod until the colour just changes to pink (light red). It is the end-point of the titration. The addition of acid is immediately stopped and the volume of the acid used up is read from the burette. Three titrations are generally done, taking 25 ml of Na_2CO_3 solution each time and the volume of the acid in each titration is read. The mean of the three readings is taken.

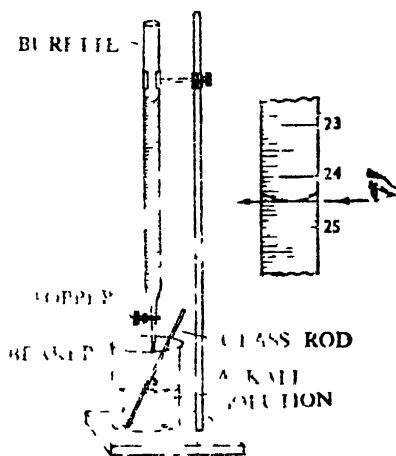


Fig. 1.26) Titration

It is the end-point of the titration. The addition of acid is immediately stopped and the volume of the acid used up is read from the burette. Three titrations are generally done, taking 25 ml of Na_2CO_3 solution each time and the volume of the acid in each titration is read. The mean of the three readings is taken.

Calculation Let the mean of the volumes of the acid used up in three titrations be 22.5 ml and the strength of the given sodium carbonate solution be $1.02 \frac{\text{N}}{10}$. The strength of the

acid is then calculated from the relation $V_1S_1 = V_2S_2$, where

V_1 - vol of the acid, S_1 - strength of the acid

V_2 - , Na_2CO_3 soln. S_2 - , Na_2CO_3 soln.

$$22.5 \times S_1 = 25 \times 1.02 \frac{\text{N}}{10}$$

$$\text{or } S_1 = \frac{25 \times 1.02 \text{ N}}{22.5 \times 10} \text{ or } 1.13 \frac{\text{N}}{10}$$

NOTE (i) It is customary to take acid in the burette. Taking of alkali in the burette is not desirable.

(ii) It is advisable to start from the zero mark on the burette. So before each titration, the acid level is to be brought to the zero mark.

(iii) Results of the titration are dependable when two consecutive burette readings are the same or when they do not differ by more than 0.1 ml.

(iv) Inner surface of the burette is washed with the given acid. This leaves it wet with the liquid it is to contain and nothing is left to contaminate the acid solution when the burette is filled. For the same reason, pipette is washed with the alkali solution.

Numerical problems on Acidimetry and Alkalimetry :

(1) What amounts of Na_2CO_3 will be required to prepare the following solutions :

- (i) 250 c.c. of 0.5 N Na_2CO_3 (ii) 500 c.c. of 0.1 M Na_2CO_3
 (iii) 1000 c.c. of 5% Na_2CO_3 ($N_a = 23$) [W.B.H.S. 1980]

(i) gm. equivalent of sodium carbonate = 53 gms.

To prepare

1000 c.c. of (N) Na_2CO_3 soln. 53 gms of Na_2CO_3 are required.

\therefore " 1000 " " 0.5N " " $\frac{53}{5}$ or 26.5 gm. " "

\therefore " 250 " " $\frac{26.5 \times 250}{1000}$ or 6.625 gm. of Na_2CO_3

are required

(ii) gm-molecular weight of $\text{Na}_2\text{CO}_3 = 106$ gms

To prepare

1000 c.c. of (M) Na_2CO_3 soln, 106 gms of Na_2CO_3 are required

\therefore 1000 " " 0.5M " " $\frac{106}{2} = 53$ " " " "

\therefore 500 " " " " " $\frac{53 \times 500}{1000}$ or 26.5 gms. of Na_2CO_3

are required

(iii) To prepare

100 c.c. of 5% Na_2CO_3 soln. 5 gms of Na_2CO_3 are required

\therefore 1000 " " " " " $\frac{5 \times 1000}{100}$ or 50 gms of " "

(2) Calculate the amount of Na_2CO_3 required to neutralise 100 ml of (N) H_2SO_4 .

100 ml of (N) $\text{H}_2\text{SO}_4 \approx 100$ ml of (N) Na_2CO_3 .

Now, 1 gm-equivalent of Na_2CO_3 = 53 gms of Na_2CO_3 .

\therefore 1000 ml of (N) Na_2CO_3 soln. contain 53 gms of Na_2CO_3 .

\therefore 100 " " " " " $\frac{53}{10}$ " " " " " Required amount of Na_2CO_3 = 5.3 gms.

(3) 25 ml of 1.12 $\frac{N}{10}$ sodium hydroxide soln. require 24.0 ml of a solution of hydrochloric acid for complete neutralisation. Calculate the strength of the acid in terms of (i) normality and (ii) gms per litre.

According to the question,

24 ml of HCl solution \approx 25 ml of 1.12 $\frac{N}{10}$ NaOH solution

Let the strength of the acid in terms of normality be x .

$$\therefore 24 \times x = 25 \times 1.12 \frac{N}{10} \quad \text{or} \quad x = \frac{25 \times 1.12 \frac{N}{10}}{24} \quad \text{or} \quad 1.166 \frac{N}{10} \quad \text{or} \quad 0.1166 (N)$$

\therefore Strength of the acid = 0.1166 (N)

and wt. in gms/litre = normality \times gm-equivalent

$$0.1166 \times 36.5 = 4.2559 \text{ gms}$$

(4) Calculate the volume of decinormal sulphuric acid soln. required to neutralise 250 ml of a solution containing 2.5 gms of caustic soda per litre ($Na = 23$)

Gm-equivalent of caustic soda = 40 gms

$$\therefore \text{Strength of the given caustic soda solution} = \frac{2.5}{40} (N) \\ = 0.0625 (N)$$

Let V ml be the volume of decinormal sulphuric acid required for neutralisation.

$$V \text{ ml of } \frac{N}{10} \text{ H}_2\text{SO}_4 = 250 \text{ ml of } 0.0625 (N) \text{ NaOH}$$

$$\therefore V \times \frac{N}{10} = 250 \times 0.0625 (N) \quad \text{or} \quad V = 250 \times 0.0625 \times 10 = 156.25 \text{ ml}$$

$$\therefore \text{Vol. of acid required} = 156.25 \text{ ml}$$

(5) A laboratory bottle containing hydrochloric acid is labelled as 12N HCl. How would you prepare 20 ml of 3N HCl taking the acid from the bottle? (W. B. H. S. 1978)

Let the required volume of the acid be x ml.

$$\therefore x \times 12N = 20 \times 3N \quad \therefore x = 5 \text{ ml.}$$

\therefore 5 ml of the acid are to be dissolved in 15 ml of water to give the acid of the desired strength.

(6) Calculate the amount (by weight) of sulphuric acid of 58% purity which will be required to prepare a litre of 0.50 (N) H_2SO_4 solution

For preparing 1 litre of (N) H_2SO_4 , we need 49 gms of H_2SO_4 .

$$\therefore \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad 0.50 (N) \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad 24.5 \quad \text{,,} \quad \text{,,} \quad \text{,,}$$

According to the question,

58 gms of H_2SO_4 are present in 100 gms of H_2SO_4

$$\therefore 24.5 \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \frac{100 \times 24.5}{58}$$

$$\text{or } 42.24 \text{ gms of } \text{H}_2\text{SO}_4$$

$$\therefore \text{wt of sulphuric acid required} = 42.24 \text{ gms.}$$

(7) A solution contains 0.4940 gm of caustic soda in 125 c.c. What is the factor of the solution if the strength be expressed as (a) N solution, (b) $\frac{N}{10}$ solution?

Gm-equivalent of NaOH = 40 gms.

(a) 125 c.c. of (N) NaOH will contain $\frac{40 \times 125}{1000}$ or 5 gms of NaOH

$$\therefore \text{factor} = \frac{0.4940}{5} = 0.0988$$

(b) 125 c.c. of $\frac{N}{10}$ NaOH solution will contain 0.5 gms of NaOH

$$\therefore \text{factor} = \frac{0.4940}{0.5} = 0.988$$

(8) 1.3456 gms of Na_2CO_3 are dissolved in water and the volume of the solution is made up to 250 c.c. 25 c.c. of this solution exactly neutralise 24.85 c.c. of a solution of H_2SO_4 . Calculate the normality of (a) Na_2CO_3 solution (b) H_2SO_4 solution

(a) 250 c.c. of Na_2CO_3 soln contain 1.3456 gms of Na_2CO_3

\therefore 1000 " " " " " " 1.3456×4 " "

$$\therefore \text{Normality of the solution} = \frac{1.3456 \times 4}{\text{Eq. wt.}} = \frac{1.3456 \times 4}{53} = 0.10155N$$

(b) Let the strength of the acid be x (N).

\therefore 24.85 c.c. of x (N) H_2SO_4 = 25 c.c. of 0.10155 (N) Na_2CO_3

$$\therefore x = \frac{25 \times 0.10155}{24.85} = 0.10216$$

\therefore Normality of the acid solution = 0.10216N

(9) One litre of a solution contains 25 gms of Na_2CO_3 . 50 ml of this solution are diluted to 250 ml. 25 ml of this diluted solution require 28 ml of a solution of sulphuric acid. Find the strength of the acid in grams per litre. (Na = 23, S = 32)

1000 ml of Na_2CO_3 solution contain 25 gms of Na_2CO_3

$$\therefore 50 \text{ " " " " " " } \frac{25 \times 50}{1000}$$

or 1.25 gms of Na_2CO_3

\therefore 250 ml of the diluted solution contain 1.25 gms of Na_2CO_3

$$\therefore \text{Strength of the diluted } \text{Na}_2\text{CO}_3 \text{ solution} = \frac{1.25}{13.25} (N)$$

(\therefore Gm-equivalent of $\text{Na}_2\text{CO}_3 = 53$ gms and 250 ml of (N) Na_2CO_3 will contain $\frac{53}{4}$ or 13.25 gms of Na_2CO_3)

Let the strength of H_2SO_4 be x (N)

\therefore According to the relation $V_1S_1 = V_2S_2$,

28 ml of x (N) $\text{H}_2\text{SO}_4 \equiv 25 \text{ ml } \frac{1}{13} \frac{25}{25}$ (N) Na_2CO_3 solution,

$\therefore \frac{25 \times 1 \cdot 25}{28 \times 13 \cdot 25}$ or strength of $\text{H}_2\text{SO}_4 = \frac{25 \times 1 \cdot 25}{28 \times 13 \cdot 25}$ (N)

wt of H_2SO_4 in one litre = Normality \times gm-equivalent

$$\frac{25 \times 1 \cdot 25 \times 49}{28 \times 13 \cdot 25} \text{ or } 4 \cdot 127 \text{ gms}$$

(10) 1.125 gm of anhydrous sodium carbonate was dissolved in water. 24.8 c.c. of a solution of sulphuric acid were required to neutralise the aqueous solution of the carbonate exactly. Calculate the normality of the acid and weight of sulphuric acid present in one litre.

1 gm-equivalent of sodium carbonate = 53 gms of Na_2CO_3

and 1 " " " " sulphuric acid = 49 " of H_2SO_4 .

Since acids and alkalis react in the ratio of their gm-equivalents,

53 gms of $\text{Na}_2\text{CO}_3 \equiv 49$ gms of H_2SO_4

$$1 \cdot 125 \text{ gm } \therefore = \frac{49 \times 1 \cdot 125}{53} \text{ or } 0 \cdot 1155 \text{ gm of } \text{H}_2\text{SO}_4$$

According to the question

24.8 c.c. of the acid solution can neutralise the whole of Na_2CO_3 solution

24.8 c.c. acid solution contain 0.1155 gm of H_2SO_4

$$1000 \therefore \therefore \frac{0 \cdot 1155 \times 1000}{24 \cdot 8} \text{ or } 4 \cdot 66 \text{ gms of } \text{H}_2\text{SO}_4$$

Strength of the acid = $\frac{4 \cdot 66}{49}$ (N) = 0.095 (N) and wt. of the

acid in gram per litre = Normality \times gm-equivalent.

$$0 \cdot 095 \times 49$$

$$= 4 \cdot 655 \text{ gms.}$$

(11) 10 c.c. of concentrated sulphuric acid of specific gravity 1.83 were diluted to one litre. 20 c.c. of this solution required 28 c.c. of 0.25 (N) NaOH solution for complete neutralisation. Calculate the percentage strength of the acid in the sample.

Wt. of 1 c.c. of the acid = 1.83 gms. (\therefore specific gravity of the acid is 1.83)

$$\therefore \text{Wt of the acid per litre of diluted acid soln.} = \frac{10 \times 1.83}{10} = 18.3 \text{ gms.}$$

Let the strength of the acid soln. be $x(N)$.

$$\therefore \text{According to } V_1 S_1 = V_2 S_2, \\ 20 \text{ c.c. of } x(N) \text{ H}_2\text{SO}_4 \equiv 28 \text{ c.c. of } 0.25 (N) \text{ NaOH soln.}$$

$$\therefore x = \frac{28 \times 0.25}{20} = 0.35 \quad \therefore \text{Strength of H}_2\text{SO}_4 \text{ soln} = 0.35(N)$$

$$\text{Wt. of the acid in gms per litre} = 0.35 \times 49 \\ = 17.15 \text{ gms}$$

$$\therefore \text{Percentage strength of the conc. acid} = \frac{17.15 \times 100}{18.3} \\ = 93.7.$$

(12) Upon heating one litre of a $\frac{N}{2}$ HCl solution, 2.675 gms of hydrogen chloride are lost and the volume of the solution shrinks to 750 ml. Calculate the normality of the resultant solution.

Gram-equivalent of HCl = 36.5 gms of HCl

$$\therefore 1 \text{ litre of } \frac{N}{2} \text{ HCl solution will contain } \frac{36.5}{2} \text{ or } 18.25 \text{ gms of HCl.}$$

$$\begin{array}{ll} \text{Hydrogen chloride lost upon heating} & - 2.675 \text{ gms.} \\ \therefore \text{ " " left in solution} & - 18.25 \text{ gms} - 2.675 \text{ gms} \\ & = 15.575 \text{ gms} \end{array}$$

1000 ml HCl solution containing 36.5 gms of HCl $\equiv 1.0N$ HCl solution

$$\therefore 750 \text{ " " " " } 36.5 \text{ " " " } \equiv \frac{1000}{750} (N) \text{ " " "}$$

$$\therefore 750 \text{ " " " " } 15.575 \text{ " " " } \equiv \frac{1000 \times 15.575}{750} N \\ \text{HCl soln.} \\ \equiv 0.5689 (N)$$

\therefore Normality of the resultant soln. 0.5689.

(13) How much water is to be added to 500 ml of a 1.2 (N) acid to make it a normal solution?

Let the required vol. of water be x ml,

$(x + 500)$ ml (N) soln $\equiv 500$ ml 1.2 (N) soln.

$$\therefore (x + 500) \times 1 = 1.2 \times 500 \quad \therefore x = \frac{1.2 \times 500}{1} - 500 = 100 \text{ ml.}$$

(14) How many c.c. of water must be added to 1 litre of 0.1088 (N) H_2SO_4 to make it exactly decinormal?

Let 1000 c.c. of 0.1088 (N) $\text{H}_2\text{SO}_4 \equiv V$ c.c. of $\frac{N}{10}$ H_2SO_4

$$\therefore 1000 \times 0.1088 N = V \times \frac{N}{10} \quad \text{or, } V = 1000 \times 0.1088 \times 10 \\ = 1088 \text{ c.c.}$$

∴ Vol of water to be added to one litre of the acid
 $= (1088 - 1000) \text{ c.c.}$
 $= 88 \text{ c.c.}$

(15) 20 c.c. of sulphuric acid solution neutralise 21.2 c.c. of 3% Na_2CO_3 solution. How would you reduce the strength of the acid to decinormal?

100 c.c. of Na_2CO_3 solution contain 3 gms of Na_2CO_3
 $\therefore 1000 \text{ ,, ,, ,, ,, } = \frac{30}{5.3} \text{ N}$
 $\therefore \text{Strength of 3\% } \text{Na}_2\text{CO}_3 \text{ soln} = \frac{30}{5.3} \left(\frac{\text{N}}{10} \right)$

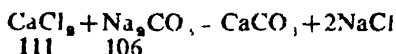
20 c.c. of H_2SO_4 soln $\approx 21.2 \text{ c.c.}$ of $\frac{30}{5.3} \left(\frac{\text{N}}{10} \right) \text{ Na}_2\text{CO}_3 \text{ soln.}$

$= 120 \text{ c.c.}$ of $\frac{\text{N}}{10} \text{ ,, ,,}$

$= 120 \text{ c.c.}$ of $\frac{\text{N}}{10} \text{ H}_2\text{SO}_4 \text{ soln.}$

∴ To reduce the strength of H_2SO_4 solution to decinormal, $120 - 20 = 100 \text{ c.c.}$ of water are required to be added to every 20 c.c. of the acid solution i.e. 5 c.c. of water are to be added to 1 c.c. of the acid solution

(16) 10 gms of CaCl_2 were dissolved in water. To this aqueous solution, 100 ml of Na_2CO_3 solution were added. After the reaction, there was no excess of Na_2CO_3 . Calculate the strength of the sodium carbonate solution in terms of normality

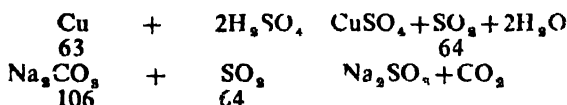


111 gms of CaCl_2 completely react with 106 gms of Na_2CO_3
 $\therefore 10 \text{ ,, ,, ,, } = \frac{106 \times 10}{111} \text{ or } 9.5 \text{ gms}$
of Na_2CO_3

100 ml of Na_2CO_3 solution contain 9.55g Na_2CO_3
 $\therefore 1000 \text{ ,, ,, } = 95.5 \text{ g ,,}$

∴ Strength of Na_2CO_3 solution $\frac{95.5}{53} = 1.8 \text{ N}$

(17) Sulphur dioxide produced by the action of 5 gms of copper on excess of conc. sulphuric acid was passed through 500 ml of $\frac{1}{2} \text{ N}$ Na_2CO_3 solution. Find out the unreacted amount of Na_2CO_3 in the solution (Cu = 63)



From the above equations,

So₂ produced from 63 gms of copper react with 106 gms of Na₂CO₃

$$\begin{array}{ccccccc} & & & & & & 106 \times 5 \\ & & & & & & 63 \\ \text{or } & 8.41 \text{ gms of Na}_2\text{CO}_3 \end{array}$$

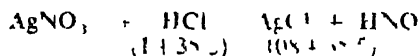
We know gm equivalent of Na₂CO₃ = 53 gms

∴ 1 litre of $\frac{1}{2}$ N Na₂CO₃ will contain = 26.5 gms of Na₂CO₃

$$500 \text{ ml, " " } \frac{26.5}{2} = 13.25 \text{ gms "}$$

So unreacted amount of Na₂CO₃ = 1.25 - 8.41 = 4.84 gms.

(18) 10 ml of a solution of HCl exactly neutralise 15 ml of a solution of NaOH. Also 10 ml of the same HCl soln when treated with excess of AgNO₃ solution gave 0.1435 gm of AgCl. Find out the strength of NaOH solution in gms/litre. (Ag = 108)



143.5 gms of AgCl are obtained from 36.5 gms of HCl

$$0.1435 \text{ gm} \quad , \quad , \quad \frac{36.5 \times 0.1435}{143.5}$$

or 0.0365 gm of HCl

∴ 10 ml of the HCl solution contain 0.0365 gm of HCl

$$1000 \text{ " " " } \frac{0.0365 \times 1000}{10}$$

or 3.65 gms of HCl

Strength of the above HCl solution = $\frac{3.65}{10} \text{ N} = 0.365 \text{ N}$ or $\frac{1}{10} \text{ N}$

Let the strength of NaOH solution be x .

So from the relation $V_1 S_1 = V_2 S_2$,

$$15 \text{ ml of } x \text{ N NaOH} = 10 \text{ ml } 0.1 \text{ N HCl}$$

$$x = \frac{10 \times 0.1}{15} = 0.0667 \text{ (N)}$$

wt of NaOH in gms/litre = Normality \times gm-equivalent
or $0.0667 \times 40 = 2.668 \text{ gms (approx)}$

(19) 30 cc of 0.2 N H₂SO₄ and 20 cc of 0.3 N H₂SO₄ were mixed together. Determine the strength of mixed acid solution.

$$30 \text{ cc. of } 0.2 \text{ (N) H}_2\text{SO}_4 = (30 \times 0.2) \text{ cc or } 6.0 \text{ cc N H}_2\text{SO}_4$$

$$20 \text{ " " } 0.3 \text{ (N) " " } = (20 \times 0.3) \text{ cc or } 6.0 \text{ cc N H}_2\text{SO}_4$$

$$\text{Vol of the mixed solution} = (30 + 20) \text{ cc or } 50 \text{ cc}$$

Let the strength of the mixed solution be x (N),

$$\therefore 50 \times x = 12.0 \times \text{N} \quad \text{or } x = \frac{12}{50} \text{ N or } 0.24 \text{ (N)}$$

(21) 25 ml of 0.08(N) sodium hydroxide solution are mixed with 20 ml of 0.09(N) sodium carbonate solution. What is the normality of the resulting alkali solution.

30 ml of the mixed alkali solution neutralise 50 ml of sulphuric acid solution. Calculate the strength of the acid in terms of normality.

Vol. of the mixed alkali solutions = $25 + 20 = 45$ ml

(supposing that there is no change in vol upon mixing)

25 ml of 0.08 (N) NaOH soln = (25×0.08) ml of (N) NaOH soln
= 2 ml of (N) NaOH soln.

20 ml of 0.09 (N) Na_2CO_3 soln = (20×0.09) ml of (N) Na_2CO_3 solution.
= 1.8 ml of (N) Na_2CO_3 soln.

Let the strength of the mixed alkali solution be x (N)

$$\therefore 45 \times x \text{ (N)} = 3.8 \text{ N}, \quad x = \frac{3.8}{45} = 0.0844$$

Strength of mixed alkali solution = 0.0844 (N)

Now, according to the question,

30 ml of 0.0844 (N) alkali soln = 50 ml of the acid soln of unknown strength

$$\therefore \text{unknown strength} = \frac{30 \times 0.0844}{50} \text{ (N)}$$

\therefore Strength of H_2SO_4 soln. = 0.05064N.

(22) 25 ml of 0.4 (N) HCl and 60 ml of 0.5 (N) H_2SO_4 were mixed together. Find the volume of 0.8 (N) NaOH solution which will be required to neutralise the mixed acid solution

25 ml of 0.4 (N) HCl soln. = (25×0.4) or 10 ml of (N) HCl soln

60 ml of 0.5 (N) H_2SO_4 soln = (60×0.5) or 30 ml (N) H_2SO_4 soln

\therefore Vol. of the (N) acid soln = $10 + 30 = 40$ ml.

Let the vol. of 0.8N NaOH soln required be V ml.

Then, according to the relation $V_1S_1 = V_2S_2$

$$40 \times (N) = V \times 0.8 \text{ (N)} \quad \text{or} \quad V = \frac{40}{0.8} = 50 \text{ ml}$$

(23) 50 ml of an alkali solution is mixed with 16 ml of a 0.75 (N) acid solution and for complete neutralisation it further requires 30 ml of 0.8 (N) sulphuric acid solution. Find the strength of the given alkali solution.

16 ml 0.75 (N) acid = (16×0.75) ml (N) acid or 12 c.c (N) acid

30 ml 0.8 (N) acid = (30×0.8) ml (N) acid or 24 ml (N) acid

\therefore total volume of (N) acid required = $(12 + 24)$ ml or 36 ml

Let the strength of the given alkali be x (N)

$\therefore 50 \text{ ml } x(\text{N}) \text{ alkali} \equiv 36 \text{ ml (N) acid}$

$$\therefore x - \frac{36}{50}(\text{N}) = 0.72 (\text{N})$$

$\therefore \text{Strength of alkali} = 0.72 (\text{N})$

(24) 10 ml of 5% NaOH solution were poured into 10 ml of 5% HCl solution. Is the resulting solution neutral? If not, calculate the strength of the acid or alkali in the resultant solution in terms of normality.

As per data given.

100 ml of NaOH solution contain 5 gms of NaOH

$\therefore 1000 \text{ ,, ,, ,, ,, } 5 \times 10 = 50 \text{ gms of NaOH}$

$\therefore \text{Strength of NaOH soln} = \frac{50}{40}(\text{N}) = 1.25 (\text{N})$

($\because 1 \text{ gm equivalent of NaOH} = 40 \text{ gms of NaOH}$)

$\therefore 10 \text{ ml of } 1.25 (\text{N}) \text{ NaOH solution} = (10 \times 1.25) \text{ ml or } 12.5 \text{ ml (N) NaOH}$

Similarly, strength of HCl soln = $\frac{50}{36.5} (\text{N}) = 1.37 (\text{N})$

($\because 1 \text{ gm-eq of HCl} = 36.5 \text{ gms}$)

$\therefore 10 \text{ ml of } 1.37 (\text{N}) \text{ HCl} \equiv (10 \times 1.37) \text{ ml or } 13.7 \text{ ml of (N) HCl}$

We know that 12.5 ml of (N) NaOH \equiv 12.5 ml of (N) HCl

But the acid solution \equiv 13.7 ml of N acid.

$\therefore \text{Excess of (N) acid} = (13.7 - 12.5) \text{ ml} = 1.2 \text{ ml}$

The resulting solution is acidic as it will contain acid equivalent to 1.2 ml of (N) HCl after the reaction.

Vol. of the resulting soln. = 10 + 10 = 20 ml.

Let the strength of the mixed solution be x (N)

20 ml of x (N) HCl soln. \equiv 1.2 ml of (N) HCl soln.

$$\text{or } x = \frac{1.2}{20}(\text{N}) = 0.06 (\text{N})$$

(25) 0.265 gm. of Na_2CO_3 is added to 50 ml of a solution of sulphuric acid of strength $\frac{\text{N}}{10}$ (factor = 1.25). Is the resulting solution acid or alkali? Calculate the volume of an acid or alkali (as the case may be) of strength $0.75 \frac{\text{N}}{10}$ required to neutralise the the resulting solution.

$$50 \text{ ml of } 1.25 \frac{\text{N}}{10} \text{ H}_2\text{SO}_4 \equiv \frac{50 \times 1.25}{10} \text{ ml or } 6.25 \text{ ml of (N) H}_2\text{SO}_4 \text{ soln.}$$

\therefore an acid and an alkali react in the ratio of their equivalents,

(28) 0.50 gm of a sample of impure calcium carbonate is dissolved in 50 ml of 0.0985 N hydrochloric acid. When the reaction is complete, the excess of hydrochloric acid requires 6.0 ml of 0.105 N caustic soda for neutralisation. Find the percentage of pure calcium carbonate in the sample.

50 ml of 0.0985 (N) HCl \equiv (50×0.0985) ml or 4.925 ml of (N) HCl

6.0 ml of 0.105 (N) NaOH \equiv (6×0.105) ml of (N) HCl

\equiv (6.0×0.105) ml or 0.630 ml (N) HCl

\therefore Vol of (N) HCl required for reaction with the impure sample
 $= (4.925 - 0.630)$ or 4.295 ml.

Gm-equivalent of $\text{CaCO}_3 = \frac{40 + 12 + 48}{2} = 50$ gms of CaCO_3

\therefore 1000 ml (N) HCl neutralise 50 grams of CaCO_3

\therefore 4.295 ml „ „ „ $\frac{50 \times 4.295}{1000}$ or 0.2147 gm of CaCO_3 .

\therefore 0.50 gm of impure sample contains 0.2147 gm of pure CaCO_3

\therefore 100 gms „ „ „ $\frac{0.2147 \times 100}{0.50}$

or, 42.94 gms of pure CaCO_3

\therefore Percentage of purity = 42.94

(29) The molecular weight of a dibasic acid is 126.

1.4175 gms of the acid were dissolved in 250 c.c. of water. 22.5 c.c. of the acid solution thus obtained neutralise completely 25 c.c. of a NaOH solution. 10 c.c. of the same NaOH solution require 8 c.c. of a solution of H_2SO_4 of unknown strength. Calculate the strength of the H_2SO_4 solution.

Eq. wt of the dibasic acid = $\frac{126}{2} = 63$

\therefore 1000 c.c. of (N) dibasic acid soln. contain 63 gms of the acid.

As per question,

250 c.c. of the dibasic acid soln contain 1.4175 gms of the acid

1000 „ „ „ „ „ „ $1.4175 \times 4 = 5.67$ gms of acid.

\therefore Strength of the dibasic acid = $\frac{5.67}{63}$ (N) = 0.09 (N)

Let the strength of NaOH soln. be x (N).

\therefore According to the relation, $V_1 S_1 = V_2 S_2$

25 c.c. x (N) NaOH \equiv 22.5 c.c. of 0.09 (N) dibasic acid

$\therefore x = \frac{22.5 \times 0.09}{25}$ or Strength of NaOH soln. = 0.081 (N)

Again, 10 c.c. of 0.081 (N) NaOH soln. \equiv 8 c.c. of H_2SO_4 soln. of unknown strength

\therefore Strength of sulphuric acid = $\frac{10 \times 0.081}{8}$ (N) = 0.1012 (N)

(30) 0.6882 gm of a dibasic acid was dissolved in water and the solution was made up to 100 ml. 20 ml of the solution when titrated against an 0.102N alkali solution required exactly 21.3 ml. Calculate the equivalent weight and the molecular weight of the acid.

From the relation $V_1 S_1 = V_2 S_2$

$$20 \times S_1 = 21.3 \times 0.102N$$

$$\therefore \text{Strength of the acid } (S_1) = \frac{21.3 \times 0.102}{20} N \text{ or } 0.1086N$$

Weight of the acid in 100 ml of the solution = 0.6822 gm.

\therefore weight of the acid per litre = $0.6822 \times 10 = 6.822$ gms.

Strength \times Eq. wt = weight of the acid per litre

$$\therefore \text{Eq. wt of the acid} = \frac{6.822}{0.1086} = 62.8$$

and the Mol. weight = 62.8×2 (basicity) = 125.6

(31) 0.091 gm of a metal was dissolved in 50 c.c. $\frac{N}{2}$ HCl and the solution diluted to 125 c.c.; 25 c.c. of the solution were neutralised by 30 c.c. of $\frac{N}{10}$ NaOH. Calculate the equivalent weight of the metal.

25 c.c. of the diluted acid \equiv 30 c.c. of $\frac{N}{10}$ NaOH

125 c.c. „ „ „ „ \equiv 150 c.c. of $\frac{N}{10}$ NaOH

\equiv 15 c.c. of (N) NaOH

\equiv 15 c.c. of (N) HCl left unused

Vol. of acid taken = 50 c.c. $\frac{N}{2}$ HCl \equiv 25 c.c. (N) HCl

\therefore Vol. of the acid reacting with the metal = $(25 - 15)$
or 10 c.c. (N) HCl.

10 c.c. of (N) HCl react with 0.091 gm of the metal

$$\therefore 1000 \text{ „ „ „ „ „ } \frac{0.091 \times 1000}{10}$$

or 9.1 gms of the metal

\therefore Eq. wt. of the metal = 9.1

(32) 2 gms of the carbonate of a bivalent metal were dissolved in 100 ml of seminormal HCl solution. The resulting solution required 50 ml of 0.2 (N) NaOH for its complete neutralisation. Calculate the equivalent weight and molecular weight of the metallic carbonate.

The carbonate reacts with a portion of 100 ml $\frac{N}{2}$ HCl

The remaining acid required 50 ml 0.2 (N) NaOH for neutralisation

Now, $100 \text{ ml } \frac{N}{2} \text{ HCl} = 50 \text{ ml (N) HCl}$

$50 \text{ ml } 0.2 \text{ (N) NaOH} \equiv 50 \text{ ml } 0.2 \text{ (N) HCl} \equiv 10 \text{ ml (N) HCl}$.

\therefore Vol. of acid left = 10 ml (N) HCl

and " " " used up by the carbonate = (50 - 10)

or 40 ml (N) HCl

$40 \text{ ml (N) HCl} \equiv 2 \text{ gms of the carbonate}$

$\therefore 1000 \text{ " " } \equiv 50 \text{ gms " " "}$

\therefore Eq. wt of the metal carbonate = 50

and mol. wt " " = $50 \times 2 = 100$

(33) 0.236 gm. of an organic dibasic acid gave on combustion 0.352 gm. of CO_2 and 0.108 gm. of water. 0.059 gm of the acid required 10 ml of $\frac{N}{10}$ barium hydroxide solution for neutralisation.

What is the molecular formula of the acid ?

44 gms. of CO_2 contain 12 gms of carbon

$\therefore 0.352 \text{ gm. " " contains } \frac{12 \times 0.352}{44} \text{ gms " "}$

% of carbon in the acid = $\frac{12 \times 0.352 \times 100}{0.236 \times 44} = 40.67 \text{ gms " "}$

Again, 18 gms of H_2O contain 2 gms of hydrogen

$\therefore 0.108 \text{ gm " " contains } \frac{2 \times 0.108}{18} \text{ " " "}$

\therefore % of hydrogen in the acid = $\frac{2 \times 0.108 \times 100}{0.236 \times 18} = 5.08$

% of oxygen (by difference) = $100 - (40.67 + 5.08) = 54.25$

$\therefore \text{C : H : O (by wt.)} = 40.67 : 5.08 : 54.25$

$\therefore \text{C : H : O (by relative number of atoms)} = \frac{40.67}{12} : \frac{5.08}{1} : \frac{54.25}{16}$
 $= 3.39 : 5.08 : 3.39$
 $= 1 : 1.5 : 1$

(Dividing by lowest number 3.39)

Simple whole number ratio is 2 : 3 : 2

\therefore Empirical formula of the acid is $\text{C}_2\text{H}_3\text{O}_2$.

10 ml of $\frac{N}{10} \text{ Ba(OH)}_2$ soln. neutralise 0.059 gm of the acid. But

1 gm-equivalent of Ba(OH)_2 must neutralise 1 gm-equivalent of the acid.

$10 \text{ ml of } \frac{N}{10} \text{ Ba(OH)}_2 \text{ soln} \equiv 1 \text{ ml of (N) Ba(OH)}_2 \text{ soln.}$

1 ml of (N) Ba(OH)_2 soln. = 0.059 gm of the acid

$1000 \text{ " " " } = 59 \text{ gms " " "}$

\therefore Equivalent weight of the acid = 59

and the molecular weight " " = Eq. wt \times basicity = $59 \times 2 = 118$

Let the molecular formula of the acid be $(C_2H_3O_2)_n$
 [n —a small whole number]

$$\therefore (C_2H_3O_2)_n \quad 118 \quad \therefore n(24+3+32) = 118 \text{ or } n=2$$

\therefore Molecular formula of the acid $C_4H_6O_4$.

(34) Exactly 20 ml of hydrochloric acid solution containing 29.2 gms per litre were required to neutralise 1.12 gms of a mixture of calcium oxide and calcium chloride. Calculate the percentage of CaO in the mixture.

1 gm-equivalent of HCl = 36.5 gms of HCl

$$\therefore \text{Normality of HCl soln.} = \frac{29.2}{36.5} = 0.8$$

We know that normality = $\frac{\text{gram-equivalent of the acid}}{\text{vol. of acid in litre}}$

The acid soln contains $0.8 \times \frac{20}{1000}$ or 0.016 gm-equivalent of the acid

Since, the neutralisation between an acid and base occurs in the ratio of their equivalents.

0.016 gm-equivalent of HCl = 0.016 gm-equivalent of CaO

(\therefore Out of CaO and $CaCl_2$ in the mixture, only CaO will react with HCl)

1 gm equivalent of CaO = $\frac{\text{Mol wt of CaO}}{\text{acidity}} = \frac{40+16}{2} = 28 \text{ gms}$

$$\therefore 0.016 \text{ gm-equivalent of CaO} = 28 \times 0.016 = 0.448 \text{ gm}$$

$$\therefore 1.12 \text{ gms of the mixture will contain } 0.448 \text{ gm of CaO}$$

$$\therefore 100 \text{ " " " " " " } = \frac{0.448 \times 100}{1.12}$$

$$\text{or } 40.7 \text{ gms of CaO}$$

$$\therefore \% \text{ of CaO} = 40.7$$

(35) 1 gm of impure sodium carbonate is dissolved in water and the solution is made up to 250 c.c. To 50 c.c of this solution, 50 c.c. of 0.1 N HCl are added and the mixture requires for neutralisation 10 c.c of 0.16 (N) NaOH solution. Determine the percentage of pure Na_2CO_3 in the given sample

$$50 \text{ c.c. of } 0.1 \text{ N HCl solution} = (50 \times 0.1) \text{ c.c. (N) HCl solution.} \\ = 5 \text{ c.c. (N) HCl solution}$$

$$10 \text{ c.c. } 0.16 \text{ (N) NaOH solution} = (10 \times 0.16) \text{ c.c. or } 1.6 \text{ c.c. (N, NaOH solution.} \\ = 1.6 \text{ c.c (N) HCl solution.}$$

$\therefore (5 - 1.6)$ or 3.4 c.c. of (N) HCl neutralise 50 c.c. of Na_2CO_3 solution. Let the strength of the Na_2CO_3 solution be x (N),

$$50 \text{ c.c. } \times (N) \text{ Na}_2\text{CO}_3 = 3.4 \text{ c.c. } (N) \text{ HCl}$$

$$\therefore x = \frac{3.4}{50} \text{ or strength of Na}_2\text{CO}_3\text{-soln.} = \frac{3.4}{50} \text{ (N)}$$

for 0 068 (N).

1 c.c. of (N) Na_2CO_3 solution contains $\frac{53}{1000}$ or 0.053 gm of

$$\text{Na}_2\text{CO}_3$$

∴ 250 c.c. 0.068 (N) Na_2CO_3 solution contain $0.053 \times 0.068 \times 250$
or 0.901 gm of Na_2CO_3 .

or 1 gm impure sample (present in 250 c.c.) contains 0.901 gm
of pure Na_2CO_3

100 gms impure sample contain 90.1 gm of pure Na_2CO_3
 % of pure Na_2CO_3 in the sample 90.1

(36) 100 gm of a mixture of anhydrous sodium carbonate and potassium carbonate was dissolved in water and the volume was made up to 250 cc. 25 cc. of this solution were neutralised by 20 c.c. of hydrochloric acid of unknown concentration. The neutral solution then required 16.24 cc. of 0.1N AgNO_3 for precipitation. Calculate the percentage by weight of K_2CO_3 in the mixture.

For precipitation, the chloride and silver nitrate react in the ratio of their equivalents

20 c.c. of HCl solution - 16.24 c.c. of 0.1 N AgNO_3 solution
- 16.24 c.c. of 0.1 N HCl solution

Strength of the HCl solution $\frac{16.24 \times 0.1}{20} \text{N}$ or 0.0812N.

Again, 25 cc of dilute alkali solution - 16.24 cc of 0.1N HCl solution.

250 cc. " " " " 16.24 cc of N HCl solution.

Equivalent weight of K_2CO $\frac{2 \times 39 + 12 + 3 \times 16}{2}$ 69

and eq. wt. of Na_2CO_3 , $\frac{2 \times 23 + 12 + 3 \times 16}{2}$ 53

Let the weight of K_2CO_3 in 1 gm of the mixture be x gm
 „ „ „ „ Na_2CO_3 „ „ „ „ $(1-x)$ gm.

Again, 69 gms of $K_2CO_3 \equiv 1000$ c c of N HCl solution

$$\therefore \quad \text{r} \quad \text{r} \quad \text{r} = \frac{1000 \times x}{69} \quad \text{r} \quad \text{r} \quad \text{r}$$

and 53 „ $\text{Na}_2\text{CO}_3 = 1000$ c.c. of NHCl solution

$$\therefore (1-x) \text{ ,, } \text{ ,, } = \frac{1000 \times (1-x)}{53} \text{ c.c. of NHCl solution}$$

(39) Upon adding 50 ml of (N)KOH solution to a solution containing 1.524 gms of NH_4Cl , the total solution was boiled till NH_3 ceased to be evolved. The resultant solution required 30.95 ml of (N) H_2SO_4 for complete neutralisation. Find the percentage of ammonia in ammonium chloride.

30.95 ml of (N) $\text{H}_2\text{SO}_4 \equiv 30.95$ ml of (N) KOH

\equiv vol of KOH soln. left unused.

\therefore Vol. of (N) KOH used up to decompose NH_4Cl to NH_3

$= (50 - 30.95) \text{ ml} = 19.05 \text{ ml}$

$\therefore 19.05 \text{ ml of (N)KOH} \equiv 19.05 \text{ ml of (N) NH}_3$

Now, eq. wt. of $\text{NH}_3 = 17$

$\therefore 1000 \text{ ml (N) NH}_3 \text{ soln. will contain } 17 \text{ gms of NH}_3$

$\therefore 19.05 \text{ ,, ,, ,, ,, ,, } \frac{17 \times 19.05}{1000} \text{ or } 0.32385 \text{ gm.}$
of NH_3

So, 1.524 gms of NH_4Cl contain 0.32385 gms of NH_3

$\therefore 100 \text{ ,, ,, ,, } \frac{0.32385 \times 100}{1.524} \text{ or } 21.25 \text{ gms of}$
 NH_3

\therefore Hence %, of $\text{NH}_3 = 21.25$

(40) A solution of caustic soda containing 4.74 gms per litre is prepared. Calculate the volume of hydrogen chloride at N. T. P. which will neutralise 60 ml of the prepared alkali solution.

(Na = 23, Cl = 35.5)

As per data given,

1000 ml of the solution contain 4.74 gms of NaOH

$\therefore 60 \text{ ,, ,, ,, } \frac{4.74 \times 60}{1000} \text{ or } 0.2844 \text{ gm of NaOH.}$

We know, 1 gm.-equivalent (or 40 gms) of NaOH neutralises 1 gm.-equivalent (or 36.5 gms of) HCl gas.

At N.T.P., 36.5 gms of hydrogen chloride occupy 22.4 litres

$\therefore 40 \text{ gms of NaOH require for neutralisation } 22.4 \text{ litres of}$
hydrogen chloride at N.T.P.

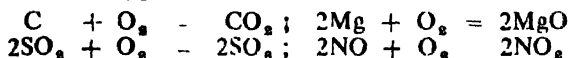
$\therefore 0.2844 \text{ gm of NaOH requires } \frac{22.4 \times 0.2844}{40} \text{ or}$

0.1592 litre of HCl

OXIDATION AND REDUCTION

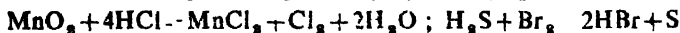
The Old Concept :

Oxidation : Ordinarily, the term oxidation is used to designate the reaction involving direct addition of oxygen to an element or a compound or increase in the proportion of oxygen in a compound. The substance with which the oxygen unites is said to be oxidised. Carbon, magnesium etc. when burnt in air take up oxygen and are oxidised into their respective oxides. Sulphur dioxide (in contact with a catalyst) and nitric oxide combine directly with oxygen producing sulphur trioxide and nitrogen dioxide respectively. In each of the latter two reaction, oxidation has increased the proportion of oxygen in the reacting oxide.



Due to its chemical nature, hydrogen is regarded as a kind of 'chemical opposite' of oxygen ; so the reaction in which hydrogen is removed (partly or wholly) from a compound is also called oxidation.

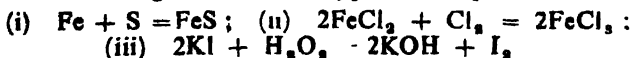
When heated, manganese dioxide and concentrated hydrochloric acid react with each other yielding chlorine. Sulphur is precipitated when hydrogen sulphide and bromine water interact. Here, hydrochloric acid and hydrogen sulphide are said to be oxidised to chlorine and sulphur respectively by giving up their hydrogen.



The definition of oxidation has further been modified in the light of the increase in our knowledge of the mode of occurrence of chemical reactions. We know that oxygen is a typical electro-negative element and hydrogen belongs to a class of elements known as electro-positive elements. Hence, the concept of oxidation has been extended logically to include all reactions involving addition of any electro-negative element and removal of any electro-positive element.

In a broader sense, oxidation is a process which introduces or increases the proportion of oxygen or any other electro-negative element or radical in a substance or removes or decreases the proportion of hydrogen or any other hydrogen like electro-positive element or radical from a substance.

The following reactions are typical examples of oxidation.

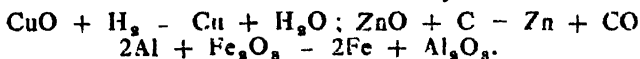


Here, in the reaction (i) between iron and sulphur, iron has been oxidised because sulphur, an oxygen-like electro-negative element has been added to it. In the reaction (ii), ferrous chloride has undergone oxidation due to the increase in the proportion of electronegative element chlorine in its molecule. The equation (iii) above reveals that the electro-positive element potassium is removed from potassium iodide causing liberation of free iodine. Hence, potassium iodide is said to be oxidised to iodine by hydrogen peroxide.

It is evident from above that there are oxidation reactions where oxygen plays no part.

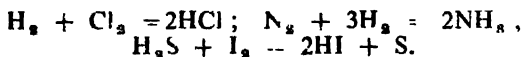
Reduction : Reduction is the reverse process of oxidation. In a restricted sense, the term reduction is used to describe the reaction which involves removal or decrease in the proportion of oxygen from a compound. Moreover, addition or increasing the proportion of hydrogen to a substance (either an element or a compound) is also called reduction. The substance which gives up oxygen or takes up hydrogen is said to be reduced.

When cupric oxide is heated in a current of hydrogen, metallic copper and water are produced. Heated zinc oxide reacts with carbon yielding metallic zinc and carbon monoxide. Ferric oxide at red heat is converted into metallic iron by aluminium.



In the above reactions, oxygen is removed from each of the oxides. Hence, these oxides have undergone reduction.

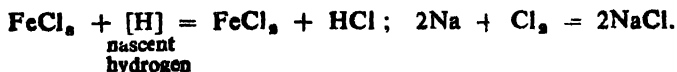
Again, hydrogen combines directly with chlorine and nitrogen to give hydrogen chloride and ammonia respectively. As a result of reaction between hydrogen sulphide and iodine, hydroiodic acid and sulphur are formed. In these cases, chlorine, nitrogen and iodine have been reduced as the three elements have combined with hydrogen.



Like oxidation, the scope of the term reduction has also been extended.

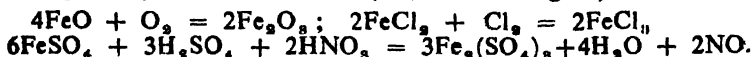
In a broader sense, reduction is a process which removes or decreases the proportion of oxygen or any other oxygen-like electro-negative element or radical from a substances or introduces or increases the proportion of hydrogen or a hydrogen-like electro-positive element or radical in a substance.

The following pair of reactions may be cited as the examples of reduction.

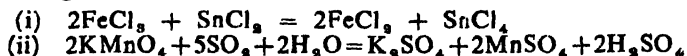


In the case of reaction between ferric chloride and nascent hydrogen, ferric chloride has suffered reduction as the proportion of electro-negative element chlorine present in it is decreased. Again, in the reaction between sodium and chlorine producing sodium chloride, chlorine is reduced because the electro-positive element sodium has been added to it.

The change of valency of an element involved in a redox reaction is to be noted. Oxidation involves increase in the positive valency (or decrease in the negative valency) of the element oxidised. In each of the following reactions, iron has been oxidised and its valency changes from +2 to +3 (*i.e.*, lower to higher).



Decrease in the positive valency (or increase in the negative valency) of an element is associated with the process of reduction, *e.g.*



In the reaction (i) mentioned above, ferric chloride has been reduced to ferrous chloride and the trivalent ferric iron is changed into divalent ferrous iron.

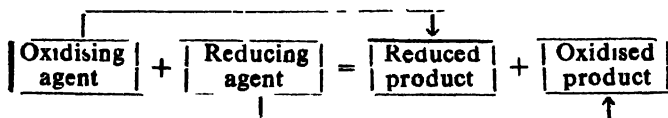
In the reaction (ii), permanganate salt has been reduced to manganous salt and during the process of reduction heptavalent manganese is converted into bivalent manganese *i.e.* change of valency of manganese is from +7 to +2 (higher to lower).

Oxidising and reducing agents : (according to old concept). The substance which in a chemical reaction supplies oxygen or any other electro-negative element to a substance or withdraws hydrogen or any other electro-positive element from a substance is called an *oxidising agent* or *oxidant*. Examples of oxidising agents are—oxygen, hydrogen peroxide, halogens, nitric acid, potassium permanganate, potassium dichromate etc.

Again, the substance which in a chemical reaction, removes oxygen or any other electro-negative element partly or wholly from a compound or supplies hydrogen or any other electro-positive element to an element or a compound is called a *reducing agent* or *reductant*. Some examples of reducing agents are—gaseous hydrogen, nascent hydrogen, hydrogen sulphide, sulphur dioxide, stannous chloride etc.

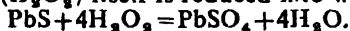
Simultaneous occurrence of oxidation and reduction : The two processes, oxidation and reduction, are complementary and must occur simultaneously. Neither an oxidation nor a reduction can take place alone. An oxidising agent brings about the oxidation of a substance and in the process it itself gets reduced. Similarly, a reducing agent is itself oxidised when it reduces a substance. In other words, an oxidising agent cannot exhibit its oxidising properties unless there is a reducing agent in the reacting system.

Such reactions are referred to as reduction-oxidation reactions or redox reactions in short.

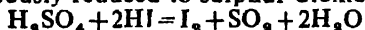


Examples : (a) When hydrogen is passed over heated cupric oxide, the latter is reduced to metallic copper by the removal of oxygen but the reducing agent hydrogen is itself oxidised to water (steam) by gaining oxygen. $\text{CuO} + \text{H}_2 = \text{Cu} + \text{H}_2\text{O}$.

(b) When hydrogen peroxide oxidises lead sulphide into lead sulphate, it (H_2O_2) itself is reduced into water.



(c) In the reaction between conc. sulphuric acid and hydroiodic acid, hydroiodic acid is oxidised to iodine by sulphuric acid which is simultaneously reduced to sulphur dioxide.



(d) Stannous chloride reduces ferric chloride into ferrous chloride by decreasing the proportion of chlorine but at the same time it is oxidised into stannic chloride by taking up chlorine.



Oxidation and reduction in the light of new electronic concept : The oxidation-reduction reaction is nowadays explained in a generalised and unrestricted way in terms of electrons. The most recent definition of oxidation-reduction process expresses the changes taking place through electron transfer from element to element in the course of chemical reaction.

From the electronic point of view, oxidation is a chemical process whereby an atom or an ion loses one or more electrons and the atom or ion that furnishes electrons in a reaction is said to be oxidised. On the other hand, reduction is the process in which an atom or an ion gains one or more electrons in the course of the reaction. The atom or ion that accepts electrons in a reaction is said to be reduced. Obviously, reduction is the exact reverse of oxidation.

From the foregoing discussions, oxidation-reduction reaction may be looked upon as a chemical reaction resulting in a change in the electrical charges on the reacting particles.

Oxidation	Reduction
$\text{Na} \rightarrow \text{Na}^+ (\text{or } \text{Na}^{+1})$	$\text{Na}^+ + e \rightarrow \text{Na}$
$\text{Zn} \rightarrow \text{Zn}^{++} (\text{or } \text{Zn}^{+2})$	$\text{Zn}^{++} + 2e \rightarrow \text{Zn}$
$\text{Fe}^{++} - e \rightarrow \text{Fe}^{+++} (\text{or } \text{Fe}^{+3})$	$\text{Fe}^{+++} + e \rightarrow \text{Fe}^{++}$
$2\text{I}^- - 2e \rightarrow \text{I}_2$	$\text{I}_2 + 2e \rightarrow 2\text{I}^- (\text{or } \text{I}^{-2})$
$\text{Cl}^- - e \rightarrow \text{Cl}$	$\text{Cl} + e \rightarrow \text{Cl}^-$
$\text{S}^{--} - 2e \rightarrow \text{S}$	$\text{S} + 2e \rightarrow \text{S}^{--} (\text{or } \text{S}^{-2})$

It is clear that oxidation results in the conversion of

- (i) a neutral metallic atom into its ion
- (ii) a metallic ion (cation) in the lower valency state (ous-ion) into an ion in the higher valency state (ic-ion)

(iii) a non-metallic ion (anion) into the non-metallic element.

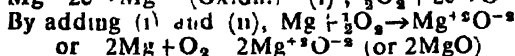
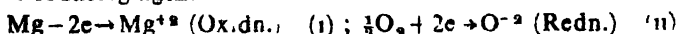
In a reverse process, reduction results in the conversion of

- (i) a non-metallic element into its ion
- (ii) an 'ic' cation into an 'ous' cation
- (iii) the metallic ion (cation) into the metal.

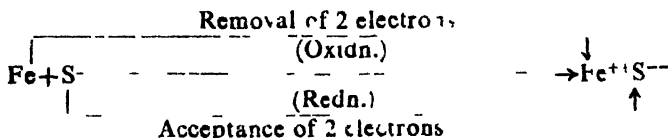
Modern definitions of oxidising and reducing agents : The substances which accept electrons and undergo reduction easily are called oxidising agents. The reducing agents are the substances which are readily oxidised by the donation of electrons.

Thus, oxidation and reduction are complementary processes of electron loss and electron gain respectively. The electrons lost by the reducing agent must be accepted by an oxidising agent present. So, in a reaction, whenever one substance is oxidised, another substance is correspondingly reduced. This leads to the conclusion that there cannot be a reaction in which only oxidation or only reduction takes place.

Examples : (a) When magnesium is burnt in air, it is converted into magnesium oxide. Here magnesium is oxidised by losing two electrons per atom. These electrons are taken up by oxygen atoms which are reduced as a result. Magnesium (donor of electrons) is the reducing agent



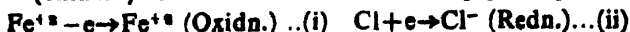
Combination of iron and sulphur to give ferrous sulphide is a similar process.



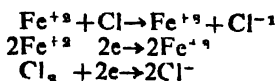
(b) When chlorine is passed through a solution of ferrous chloride, the latter is converted into ferric chloride. This reaction is expressed by the molecular reaction as



According to the ionic theory, this reaction is primarily a reaction between Fe^{+2} ions and chlorine and the above equation may be written ionically. Each ferrous ion Fe^{+2} (reductant) is oxidised to ferric ion, Fe^{+3} by losing one electron and the neutral chlorine atom (oxidant) is reduced to chloride ion by gaining the electron.



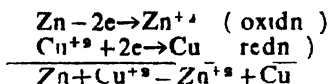
Here, the number of electrons lost by each Fe^{+2} ion is equal to the number of electrons gained by a chlorine atom. So, by adding equations (i) and (ii), we get



∴ The complete reaction $2\text{Fe}^{+2} + \text{Cl}_2 = 2\text{Fe}^{+3} + 2\text{Cl}^{-}$

(c) When zinc is added to a solution of copper sulphate, copper is precipitated and zinc goes into the solution in the form of zinc sulphate $\text{Zn} + \text{CuSO}_4 = \text{ZnSO}_4 + \text{Cu}$

Ionically,



Here, copper gains two electrons lost by zinc. Hence, copper is reduced and zinc is oxidised

(d) The reduction of hot cupric oxide by hydrogen is expressed as $\text{Cu}^{+2}\text{O}^{-2} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$

It is evident that cupric ion, Cu^{+2} is reduced by electron gain as $\text{Cu}^{+2} + 2e \rightarrow \text{Cu}$

The electrons are made available by the interaction between the oxide ion, O^{-2} and a molecule of hydrogen consisting of two atoms $\text{O}^{-2} + \text{H}_2 \rightarrow \text{H}_2\text{O} + 2e$

Thus, by combining with oxygen in this way and supplying electrons to the metallic ion, hydrogen shows reducing properties. The oxide ion is oxidised by electron loss and the oxygen remains in combination with hydrogen as water

(e) When a solution of ferric chloride is treated with a solution of stannous chloride, ferric chloride is reduced to ferrous chloride while stannous chloride is oxidised to stannic chloride



In this reaction, Fe^{+3} and Sn^{+2} actually react, the chloride ions, Cl^{-} play no part

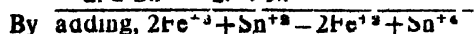
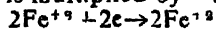
Here, each ferric ion, Fe^{+3} (oxidant) gains one electron and is reduced to ferrous ion, Fe^{+2}



Each stannous ion, Sn^{+2} (reductant) on the other hand is oxidised to stannic ion, Sn^{+4} by releasing two electrons,



As the number of electrons lost by a reductant must be the same as the number of electrons captured by an oxidant, the partial equation (i) is multiplied by 2. Now,



Similarly, the following oxidation-reduction reactions are expressed in terms of electrons. (i) $2KI + Cl_2 = 2KCl + I_2$

Partial equation for the oxidising agent $Cl_2 + 2e \rightarrow 2Cl^-$ (i)

" " " " reducing agent $2I^- - 2e \rightarrow I_2$ (ii)

(2) By adding (i) & (ii) $2I^- + Cl_2 = I_2 + 2Cl^-$

$Br_2 + H_2S = 2HBr + S$

Partial equation for oxidising agent $Br_2 + 2e \rightarrow 2Br^-$ (i)

" " " " reducing agent $H_2S - 2e \rightarrow 2H^+ + \overset{0}{S} \dots$ (ii)

Adding (i) and (ii) $Br_2 + H_2S = 2H^+ + 2Br^- + S^0$

S^0 indicates the electrical neutrality of sulphur. An element in the uncombined state is considered to have zero valency.

The complete rules for balancing equations in terms of electrons (Ion-Electron method) may be expressed as follows :

(a) First of all the products of the reactions are to be ascertained. (b) Next partial equation for the oxidising agent (showing acceptance of electrons) is to be set up. (c) Then, partial equation for the reducing agent giving out electrons is to be written in the same way. (d) Each partial equation (if required) is then multiplied by a suitable number so that when the two are added the electrons just cancel out. (e) The two partial equations are added and the substances which appear on both sides of the equation are cancelled.

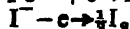
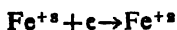
Experiment to show the electron-transfer in the reaction between ferric sulphate solution and potassium iodide solution :

That an oxidation-reduction process occurs with the transfer of electrons can be experimentally demonstrated in some cases. Let us consider the reaction between ferric sulphate and potassium iodide solutions.

To a few ml of ferric sulphate solution in a test tube, a few drops of potassium iodide solution are added. The brown colour of iodine will appear throughout the solution.

Molecular equation : $Fe_2(SO_4)_3 + 2KI = 2FeSO_4 + K_2SO_4 + I_2$

Expressed in ionic form to illustrate electron transfer, this equation becomes :



Here, an electron is transferred from the iodide ion to the ferric (Fe^{+3}) ion. The iodide here reduces the ferric compound to ferrous compound.

The same reaction may be brought about without mixing up the two solutions, as follows.

Potassium iodide solution and ferric sulphate solution are taken in two separate beakers. Each solution has a platinum electrode dipping into it. Now the two electrodes are joined to a sensitive voltmeter. The solutions in the two beakers are connected with a strip of filter paper soaked in common salt solution. This is known as a salt-bridge which completes the circuit. On careful observation, it is found that the brown colour of iodine appears in the beaker

containing potassium iodide solution. This indicates that iodide ions are being oxidised to iodine. Since there is no direct current supply in the circuit, there is no electrolysis taking place, nor do the two solutions come into contact. Because the salt-bridge completes a full electrical circuit, the electrons given up by the iodide ions are able to transfer to the Fe^{+3} ions in the other beaker and thereby carry out the reduction of ferric ions. The appearance of iodine around the electrode in the potassium iodide solution is a further indication of the part played by the electrons in this process.

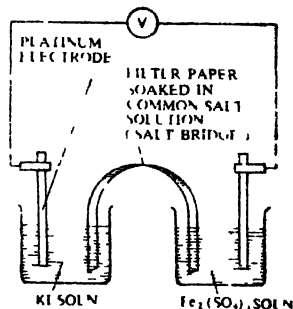
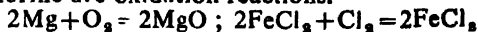


Fig. 1(27) Electron transfer in a redox reaction

Inter-relation between the old and the new concepts of oxidation and reduction: On careful examination, it is revealed that there is no fundamental difference between the old and the new concepts of oxidation and reduction. In support of this, some typical oxidation-reduction reactions are explained below in the light of earlier ideas and from the present electronic point of view.

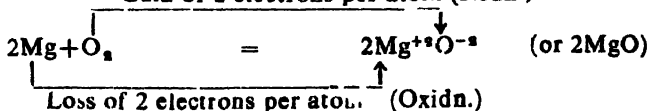
The combination of magnesium and oxygen giving magnesium oxide and the conversion of ferrous chloride into ferric chloride by chlorine are oxidation reactions.



According to the earlier concept, magnesium is oxidised to its oxide by addition of oxygen and oxygen is reduced simultaneously because it has combined with the electro-positive element magnesium. Similarly, ferrous chloride gets oxidised into ferric chloride as a result of increase in the proportion of electro-negative element chlorine and chlorine has undergone reduction due to the addition of electro-positive element iron.

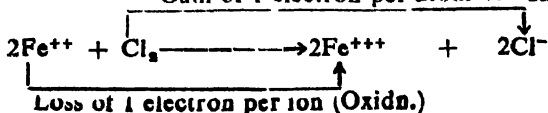
According to the new idea, a neutral magnesium atom is oxidised to a magnesium ion, Mg^{+2} by the loss of two electrons and the oxygen atom gets reduced by gaining two electrons lost by magnesium.

Gain of 2 electrons per atom (Redn.)



Again, the reaction between ferrous chloride and chlorine can be expressed ionically as follows:

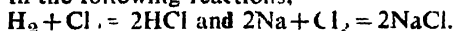
Gain of 1 electron per atom (Redn.)



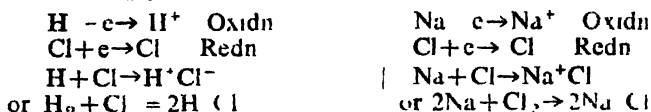
It is clear that in the old definition of oxidation, the name of the non-metal or the electronegative element (acceptor of electrons) the addition or increase in the proportion of which causes oxidation of a substance is mentioned. But according to present views, oxidation is a process of electron loss and the name of the electron-acceptor may be kept silent.

According to the modern concept, reduction is a process of electron-gain. The name of the metal (including hydrogen) or the electropositive element, electron donor, causing reduction of a substance need not be mentioned always.

In the following reactions,



Chlorine in both the cases is reduced as it has combined with hydrogen in the former reaction and with the electropositive element sodium in the latter. In terms of electron transfer these reactions can be simply expressed as,

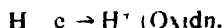


In both the cases a neutral chlorine atom has been reduced to a chloride ion, Cl^- by accepting one electron.

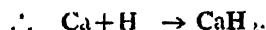
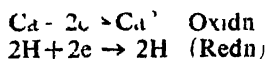
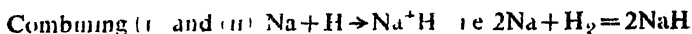
Although the old concept is correct in explaining the phenomena of oxidation and reduction the definitions of these terms in the light of electron-transfer are more general and unrestrictive. The electronic concept gives a better insight into the redox process and explains satisfactorily—

- i) the formation of anions from nonmetals
- ii) the formation of neutral metallic atoms from cations
- iii) formation of cations from metals
- iv) formation of neutral non metallic atoms from anions
- v) and reduction and oxidation of ionic species

Behaviour of hydrogen in metallic hydrides Generally hydrogen is oxidised by giving up its electron and hence acts as a reducing agent.



But in metallic hydrides like sodium hydride NaH , calcium hydride CaH_2 etc., hydrogen is converted into hydride ion by accepting electron and consequently behaves as an oxidising agent



Oxidation number. Although most of the reactions involving oxidation and reduction can be explained satisfactorily in terms of electron-loss and electron-gain, there are redox reactions where direct transfer of electron or electrons does not take place in the true sense. Consequently, such reactions cannot be easily expressed in the light of electrons.

To extend the idea of electron-transfer in all cases of oxidation, a new concept has been introduced. This is the concept of oxidation number or oxidation state.

An atom forms its ion either by losing or gaining electron or electrons. When the atom loses electrons, it undergoes oxidation producing the positive ion or cation while by gaining one or more electrons, the atom suffers reduction with the formation of negative ion or anion. The positive ion of an element is its oxidised state and the negative ion is the reduced state or negative oxidation state of the element from which the ion is obtained. The element in the free state is regarded as in the zero oxidation state. Therefore, the oxidation state of an element in a particular compound is determined by the number of electrons lost or gained by its atom during the formation of the compound. The term oxidation number is applied to signify the oxidation state of the element in its compounds. If the atom loses electrons or undergoes oxidation in forming the compound its oxidation number is positive. An atom will have negative oxidation number when it gains electrons or undergoes reduction in the formation of its compound.

The concept of oxidation number is the direct development of the fact that in an oxidation-reduction reaction simultaneous increase in valence (oxidation) of one element and decrease in valence (reduction) of another take place. It will be seen shortly that all redox reactions are attended by the changes of oxidation number. This is why oxidation number is sometimes referred to as the valence number.

The concept of oxidation state or oxidation number can easily be applied to cases of ionic compounds. Thus in the formation of magnesium oxide, magnesium atom loses two electrons which are accepted by one atom oxygen. Hence, magnesium oxide may be written as $Mg^{+2}O^{-2}$. So in the compound magnesium oxide, the oxidation number of magnesium is +2 and that of oxygen is -2. Similarly, in the formation of ferric chloride, an atom of iron loses three electrons which are captured by three atoms of chlorine. Hence, the oxidation state or oxidation number of iron is +3 and that of chlorine is -1.

In the formation of covalent compounds no direct transfer of electrons takes place between the constituent atoms and the concept of oxidation state in its true sense cannot be applied in such cases. However, the idea of oxidation state has been extended in cases of both ionic and non ionic compounds.

The oxidation number of an element in a particular compound may be defined as the net electric charge an atom of the element would bear if usual electron-transfer occurs due to the mutual oxidation and reduction of all the atoms constituting the molecule of the compound.

Generally, the oxidation number of an element is similar to its valency. But whereas valency is a specific term defining the combining capacity of an element with other elements, the oxidation number is an obscure term. It is arbitrarily assigned to an atom in a compound and denotes the electric charge the atom would acquire when it is in the form of its ion. The main difference between the two terms is that valency is always represented by a positive number but the oxidation number may be expressed by either positive or negative value.

It is customary to put the oxidation number with + or - sign on the top of the element to which it is assigned.

Rules for fixing oxidation number :

The oxidation number of an element in its compounds is determined according to certain rules which are stated below.

(i) The oxidation number of all elements in the free state (that is, uncombined with any other element) is zero. e.g. $\overset{0}{\text{Mg}}$, $\overset{0}{\text{S}}$, $\overset{0}{\text{Cl}_2}$, $\overset{0}{\text{N}_2}$ etc.

(ii) The algebraic sum of the oxidation numbers of all the atoms constituting the molecule of a compound is always equal to zero.

(iii) The oxidation number of hydrogen in the combined state is always +1 e.g. $\overset{+1}{\text{H}_2}\overset{+6}{\text{S}}\overset{+4}{\text{O}_4}$, $\overset{+1}{\text{H}}\overset{+1}{\text{Cl}}$ etc.

Exception : In an ionic hydride like lithium hydride or sodium hydride the oxidation number of hydrogen is -1. e.g. $\overset{+1}{\text{Li}}\overset{-1}{\text{H}}$, $\overset{+1}{\text{Na}}\overset{-1}{\text{H}}$

(iv) The oxidation number of a metal is positive in all its compounds.

(v) Oxygen in its compounds is normally assigned an oxidation number of -2 e.g. $\overset{+2}{\text{Cu}}\overset{-2}{\text{O}}$, $\overset{+1}{\text{H}_2}\overset{-2}{\text{O}}$, $\overset{+6}{\text{S}}\overset{-2}{\text{O}_3}$.

Exception—(1) In hydrogen peroxide or in other peroxides, the oxidation number of oxygen is -1. e.g. $\overset{+1}{\text{H}_2}\overset{-1}{\text{O}_2}$, $\overset{+1}{\text{Na}_2}\overset{-1}{\text{O}_2}$, $\overset{+2}{\text{Ba}}\overset{-1}{\text{O}_2}$.

(2) In F_2O , the oxidation number of oxygen is +2 because fluorine is more electronegative than oxygen.

On the basis of the above rules, the oxidation number of an atom of any element in a compound can be easily calculated when the oxidation numbers of atoms of other elements are known. The following are a few illustrative examples.

(i) Calculation of oxidation number of S in H_2SO_4 : The oxidation numbers of hydrogen and oxygen are +1 and -2 respectively. If x be the oxidation number of S, then

$$2 \times (+1) + x + 4 \times (-2) = 0 \text{ or } x = 6 \text{ (oxidn. number of S)}$$

(ii) Oxidation number of Mn in KMnO_4 and K_2MnO_4 : The oxidation number of potassium and oxygen are +1 and -2 respectively. If x be the oxidation number of Mn in KMnO_4 , then

$$1 + x + 4 \times (-2) = 0 \quad \therefore x = +7 \text{ (oxidn. number of Mn)}$$

Similarly, it can be shown that the oxidation number of Mn in K_2MnO_4 is 6.

(iii) Oxidation number of Cl in KClO and KClO_4 :

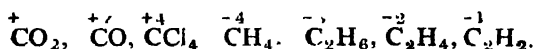
The oxidation of K = +1 and that of O = -2, If x be the oxidation number of Cl in KClO

$$1 + x + (-2) = 0 \text{ or } x = +1 \text{ (oxidn. number of Cl in KClO)}$$

In a similar manner, oxidation number of Cl in KClO_4 may be calculated to be +7

Some elements (both metals and non metals) like chromium, iron, nitrogen, sulphur etc. are capable of existing in several oxidation states or have several oxidation numbers. The oxidation numbers of carbon in its various compounds are from -4 to +4. e.g.

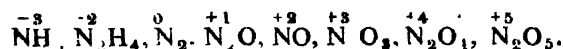
Oxidn. nos. of C



Oxidn nos. of Cr : $^+ \text{Cr}_2\text{O}_3, ^+ \text{K}_2\text{Cr}_2\text{O}_7$

„ „ „ Fe : $^+ \text{FeCl}_2, ^+ \text{FeCl}_3$

Oxidn. nos. of N :



Oxidn. nos. of S : $^- \text{H}_2\text{S}, ^+ \text{SO}_2, ^+ \text{SO}_3, ^+ \text{Na}_2\text{S}_2\text{O}_3$

The oxidation numbers of Mn in MnO_2 , KMnO_4 and K_2MnO_4 are +4, +7 and +6 respectively.

It is seen that in some higher oxides such as Fe_3O_4 , Pb_3O_4 etc. the oxidation number of the metal is not a whole number.

Let the oxidation number of Fe in Fe_3O_4 be x . Now the oxidation number of oxygen is -2.

$$\therefore 3x + 4 \times (-2) = 0 \text{ or } 3x = 8$$

$$\text{or } x = \frac{8}{3} = 2.66 \text{ (oxidn. number of Fe)}$$

The oxidation number of oxygen in potassium super oxide (KO_2) is 0.5. It is also seen that in some compounds, one of the constituent

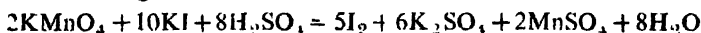
elements may have oxidation number equal to zero. Let the oxidation number of carbon in glucose, $C_6H_{12}O_6$ is x . Now, the oxidation numbers of hydrogen and oxygen are $+1$ and -2 respectively. So,

$$6x + 1 \times 12 + (-2 \times 6) = 0 \quad \therefore x = 0$$

i.e. in glucose, the oxidation number of C is zero. Similarly, it can be shown that the oxidation number of carbon in formaldehyde (CH_2O) or cane sugar $C_{12}H_{22}O_{11}$ is zero.

Oxidation and reduction in terms of oxidation number : The terms oxidation and reduction may be redefined in terms of oxidation number.

Oxidation is a process which raises the oxidation number of one of the constituent elements of the substance which is oxidised while **reduction** brings a corresponding fall in the oxidation number of one of the elements constituting the substance which suffers reduction. For example, in the redox reaction between potassium iodide solution and an acidified solution of potassium permanganate, potassium iodide is oxidised to free iodine and potassium permanganate gets reduced to manganous salt.

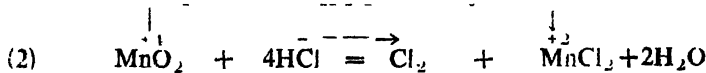
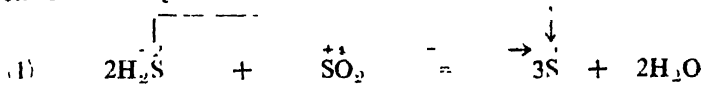


Here, oxidation numbers of iodine atom in KI and I_2 are -1 and 0 respectively

\therefore increase in oxidn. no. by $+1$ unit ($-1 \rightarrow 0$)

Conversely, oxidation numbers of Mn in $KMnO_4$ and $MnSO_4$ are $+7$ and $+2$ respectively. \therefore Decrease in oxidn. number by $+5$ units ($+7 \rightarrow +2$).

Similar increase and decrease in oxidation numbers of the elements oxidised and reduced may be illustrated by the following reactions involving oxidation and reduction.



Balancing of equations by Oxidation number . We know that oxidation is the algebraic increase in the oxidation number of an element and conversely reduction causes a decrease in the oxidation number of an element.

It is also known that in a redox reaction, the increase in oxidation number of the element due to oxidation must be equal to the decrease in oxidation number of the element suffering reduction. To balance the equations of redox reactions by oxidation number method, the following steps are followed.

(i) Correct formulae of the oxidant and reductant and those of the products are written in the form of a skeleton (unbalanced) equation.

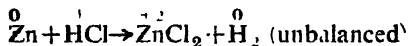
(ii) The key-element* in the oxidising agent is selected and decrease in the oxidation number of it in the reaction is calculated. Let the number showing the decrease be x .

(iii) The key-element in reducing agent is then chosen and the increase in the oxidation number of the element is similarly found out. Let the number showing the increase be y . To make the total changes in oxidation numbers of the key-elements equal, the oxidising and the reducing agents must react in the molecular ratio $x : y$, i.e. the change in oxidation number of the key-element of the oxidising agent is used as a coefficient of the reducing agent and vice versa. If any common factor is present, it is cleared out.

(iv) The coefficients of other molecules and ions which do not suffer oxidation or reduction are adjusted as and when required to get the balanced equation.

The method of balancing equations of redox reactions by oxidation number is illustrated by the following examples. The oxidation number of the element in a compound undergoing oxidation or reduction is indicated by putting the same with necessary positive or negative sign on the top of the element.

(A) In the reaction of metallic zinc and dilute hydrochloric acid, zinc reduces the acid to hydrogen and the metal is oxidised into zinc chloride by taking up the electronegative element, chlorine.

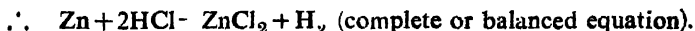


In this reaction, the oxidation number of zinc in the metallic state is 0 and that in ZnCl_2 is +2.

Increase in oxidation number of zinc due to oxidation is 2 units (from 0 \rightarrow +2)

Similarly the decrease in oxidation number of hydrogen due to reduction is 1 unit (+1 \rightarrow 0)

Therefore, Zn and HCl should react in the molecular ratio 1 : 2 to make the changes in oxidation number equal in two cases. It is obvious that there must be two 2 hydrogen atoms (2 molecules of HCl) on the left side of the equation.



(B) Carbon on being heated with conc. sulphuric acid is oxidised to carbon dioxide and sulphuric acid is reduced to sulphur

*The key-element means the element which shows variable valency in its various compounds.

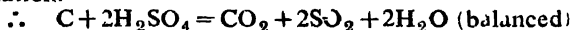
dioxide at the same time. In this redox reaction, acid is the oxidant, the key-element of which is sulphur ; carbon is the reductant.



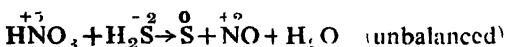
Here, oxidation number of carbon in the free state is 0 but the oxidation number of the element in carbon dioxide is +4. So the oxidation number of carbon atom is increased by +4 units (0 → +4). Again, the oxidation number of sulphur changes from +6 in H_2SO_4 to +4 in SO_2 . Thus, S suffers a decrease of +2 units (+6 → +4) in oxidation number. To equalise the increase and decrease in oxidation number, C and H_2SO_4 should react in 1 : 2 molar proportion.



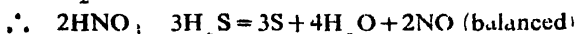
Here, 2 molecules of H_2SO_4 will give 2 molecules of SO_2 , So, to get the balanced equation, the number of oxygen atoms and that of hydrogen atoms will have to be kept equal in both sides of the equation.



(C) Dilute nitric acid oxidises hydrogen sulphide to sulphur and it itself is reduced to nitric oxide



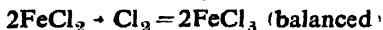
Here, decrease in oxidation number of nitrogen = +3 (5 → +2) and increase in oxidation number of sulphur = 2 (2 → 0). In order to make the total changes in oxidation number of the two elements equal, 2 atoms of nitrogen and 3 atoms of sulphur are required. i.e. HNO_3 and H_2S should react in the molecular ratio 2 : 3.



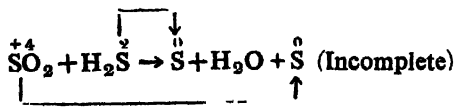
(D) Ferrous chloride on being treated with chlorine is oxidised to ferric chloride.



In the above reaction, the oxidation number of Fe in FeCl_2 is +2 and that in FeCl_3 is +3. Therefore, the increase in oxidation number of Fe due to oxidation = +1 (+2 → +3). In a similar way, it can be shown that the oxidation number of chlorine has been decreased by -1 (0 → -1). Since 1 molecule of chlorine (i.e. 2 atoms of chlorine) is involved, FeCl_2 and Cl_2 should react in the molecular ratio 2 : 1 so as to make the total changes in oxidation number of the two elements equal. Thus,



(E) Sulphur dioxide oxidises hydrogen sulphide to elementary sulphur and it itself is reduced to the same element

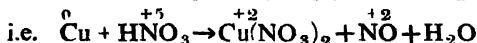


Here, decrease in oxidation number of S of $\text{SO}_2 = 4$ units ($+4 \rightarrow 0$) and increase in oxidation number of S of $\text{H}_2\text{S} = 2$ units ($-2 \rightarrow 0$)

\therefore To make the changes in oxidation number equal, two molecules of H_2S are required.

\therefore Balanced equation is $\text{SO}_2 + 2\text{H}_2\text{S} = 3\text{S} + 2\text{H}_2\text{O}$

(F) To balance the following equation by oxidation number method : $\text{Cu} + \text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + \text{NO} + \text{H}_2\text{O}$



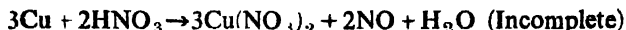
Here, Cu is oxidised (due to increase in oxidation number)

and N is reduced (due to decrease in oxidation number).

Increase in oxidation number of Cu = 2 units ($0 \rightarrow +2$)

Decrease „ „ „ „ N = 3 units ($+5 \rightarrow +2$)

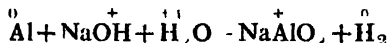
To equalize the increase and decrease in oxidation number. Cu and HNO_3 should react in the molecular ratio 3 : 2 i.e.



Since, 3 molecules of $\text{Cu}(\text{NO}_3)_2$ contains $6(\text{NO}_3)$ radicals, six more molecules of HNO_3 will be required to balance the equation.

The balanced reaction is $3\text{Cu} + 8\text{HNO}_3 = 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$

(G) When aluminium powder is added to heated caustic soda solution, sodium aluminate and gaseous hydrogen are formed.



Here, Al is oxidised (due to the increase of oxidation number) and H atoms of NaOH and water have undergone reduction (due to the decrease in oxidation number).

Increase in oxidation number of aluminium = 3 units ($0 \rightarrow +3$)

Decrease in oxidation number of H of NaOH = 1 unit ($+1 \rightarrow 0$)

and decrease in oxidation number of 2H atoms = 2 units ($+1 \rightarrow 0$)

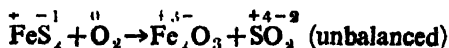
\therefore Total decrease in oxidation number = 1 + 2 or 3 units

\therefore Al, NaOH and H_2O should react in the molecular ratio 1 : 1 : 1 so that the total changes in the oxidation number become equal i.e. $\text{Al} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{NaAlO}_2 + \text{H}_2$ (unbalanced)

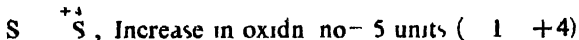
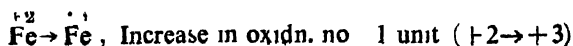
To get equal number of H atoms on both sides of the equation, the reactants must react in the molecular ratio 2 : 2 : 2.

\therefore $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} = 2\text{NaAlO}_2 + 3\text{H}_2$ (balanced)

(H) Iron disulphide on being heated with oxygen is oxidised into ferric oxide.



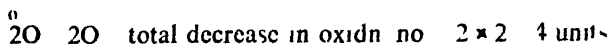
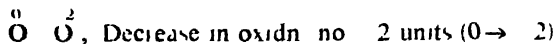
Here, both the constituents Fe and S of FeS_2 molecule have suffered oxidation.



Increase in oxidn. no for 2 S atoms = $2 \times 2 = 4$ units

\therefore Total increase in oxidn. no for each molecule of $\text{FeS}_2 = 1 + 4 = 5$ units

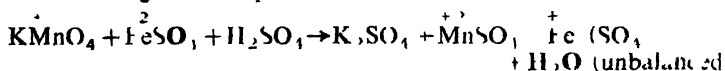
Again,



\therefore FeS_2 and O should react in the molecular proportion 4 : 1 in order to make the changes in oxidation number equal

\therefore The balanced equation is $4\text{FeS}_2 + 11\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$

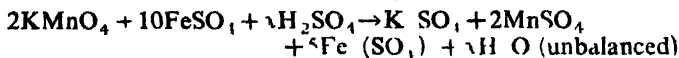
(I) As a result of reaction between ferrous sulphate and potassium permanganate in dilute sulphuric acid solution, ferrous sulphate is oxidised to ferric sulphate and permanganate is simultaneously reduced to manganous sulphate



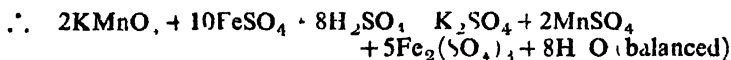
Here decrease in oxidation number of Mn due to reduction is 5 units ($+7 \rightarrow +2$) and increase of oxidation number of Fe due to oxidation is 1 unit ($+2 \rightarrow +3$)

The total changes in the oxidation number of the two elements become equal when KMnO_4 and FeSO_4 react in the molecular ratio 1 : 5.

Now, one of the products ferric sulphate $\text{Fe}_2(\text{SO}_4)_3$, contains 2 atoms of iron in its single molecule. So, to get a balanced equation, the molecular ratio must be multiplied by 2. Thus,



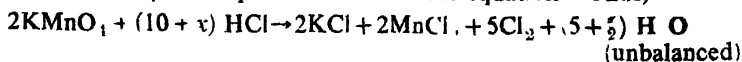
On careful scrutiny, it is found that when λ is assigned a numerical value of 8 we get the balanced equation



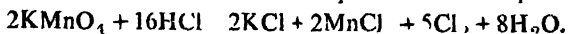
(J) Potassium permanganate oxidises conc. hydrochloric acid to chlorine and it itself undergoes reduction forming manganous salt



Here, oxidation number of Mn in KMnO_4 (oxidant) has been decreased by +5 units ($7 \rightarrow +2$), and oxidation number of Cl in HCl (reductant) is increased by +1 unit ($-1 \rightarrow 0$), therefore KMnO_4 and HCl should react in the molecular ratio 1 : 5 to make the total changes in oxidation numbers of Mn and Cl equal. Again the molecule of chlorine consists of two atoms and the above ratio should be multiplied by 2 i.e. the reactants should react in the molecular ratio 2 : 10. Since KCl and MnCl_2 are the two products formed from KMnO_4 , some more chlorine atoms (i.e. some more HCl molecules) are required to balance the equation. Thus,

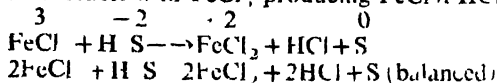


On careful scrutiny of the above equation, it is revealed that the value of x is 6. Therefore, the complete balanced equation is

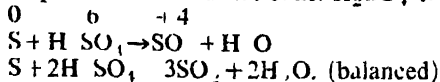


A few more examples of balancing equations by oxidation number method :

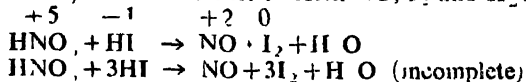
(a) H₂S reacts with FeCl_3 , producing FeCl_2 , HCl and S.



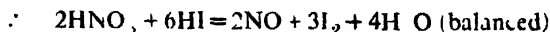
(b) Sulphur reacts with hot conc. H_2SO_4 to form SO_2 and H_2O



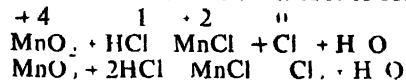
(c) HNO_3 and HI interact to form NO, I_2 and H_2O .



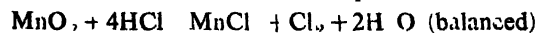
Since 3 molecules of I_2 are liberated, 6 HI molecules are required.



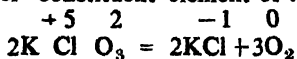
(d) MnO_2 reacts with hot conc. HCl to form MnCl_2 , Cl₂ and H_2O .



Since the right hand side of the equation contains two chloride ions, two more molecules of HCl are required

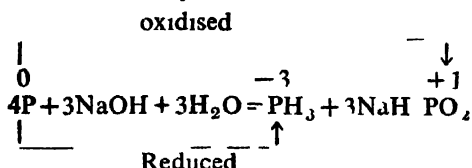


Sometimes, one constituent element of a substance is oxidised while another constituent element of the same substance is reduced
e. g.

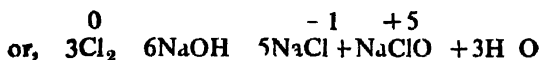
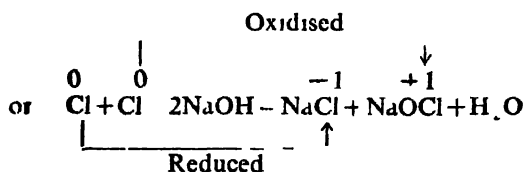


In KClO_3 , the oxidation numbers of chlorine and oxygen are $+5$ and -2 respectively. Again, the oxidation number of chlorine in KCl is -1 and that of oxygen in O_2 is 0 . So, in this reaction, the oxidation number of chlorine has been decreased ($+5 \rightarrow -1$) and that of oxygen has been increased ($-2 \rightarrow 0$). Here, chlorine of KClO_3 has undergone oxidation. On the other hand, oxygen of the same compound has suffered reduction. So the above reaction is undoubtedly a redox reaction.

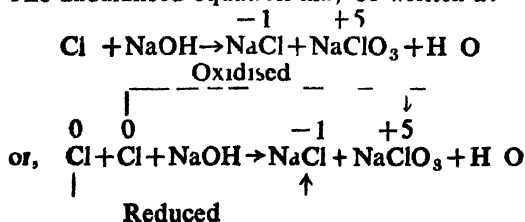
It is also to be noted that there are some reactions as shown below where a single chemical substance is converted into two products, one of which is the oxidised product and the other is the reduced one. This type of oxidation-reduction reaction is called disproportionation. White phosphorus when heated with caustic soda solution is reduced to phosphine (PH_3) and is simultaneously oxidised to sodium hypophosphite (NaH_2PO_2). This redox reaction will be clearly understood if the changes in oxidation number of phosphorus are carefully noted.



Some more reactions of this type are given below



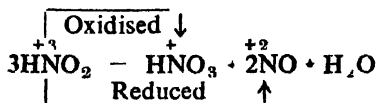
The unbalanced equation may be written as



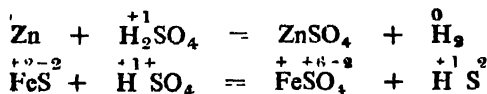
Here, the oxidation number of chlorine has decreased by 1 unit ($0 \rightarrow -1$) in the formation of NaCl and the same has increased by 5 units ($0 \rightarrow +5$) in forming NaClO_3 . So, to make the changes in oxidation number equal, the products NaCl and NaClO_3 should be in the molecular proportion 5 : 1. Now, for oxidation 5 atoms of chlorine and for reduction 1 atom of chlorine are required. So, 6 atoms or 3 molecules of chlorine are involved in the reaction. Again for the formation of 5 molecules of NaCl and 1 molecule of NaClO_3 , six atoms of Na are required i.e. 6 molecules of NaOH are required.

\therefore the balanced equation is $3\text{Cl}_2 + 6\text{NaOH} = 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$

(c) Nitrous acid (HNO_2) on long standing or heating decomposes into nitric acid (HNO_3) and nitric oxide (NO).

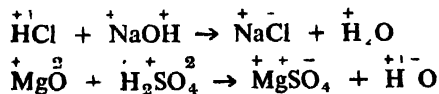


If no constituent element of the reactant or the reactants suffers any change in the oxidation number, the reaction does not fall under the category of redox reactions. Zinc and ferrous sulphide react separately with dilute sulphuric acid giving hydrogen and hydrogen sulphide.



In the first equation, the oxidation numbers of both zinc and hydrogen are changed. So, it is a redox reaction, the second equation does not represent a redox reaction as the oxidation numbers of all the elements have remained unaltered.

A neutralisation process is never a redox reaction since no change of any of the constituent elements of the acid and the base occurs.



From the above discussions, the terms oxidation and reduction may be defined completely in the following manner.

Oxidation : Oxidation is the process in which (i) oxygen or any other electronegative element or a radical is added to a substance, (ii) the positive valency of an element or a radical is increased, (iii) hydrogen or any other electronegative element or a radical is removed from a substance, (iv) an atom, ion or a molecule loses one or more electrons, (v) algebraic increase in the oxidation number of an element takes place.

Reduction: Reduction is the process in which (i) hydrogen or any other electro positive element or a radical is added to a substance, (ii) the positive valency of an element is decreased, (iii) oxygen or any other electronegative element or radical is removed from a substance, (iv) an atom or ion gains one or more electrons, (v) decrease in the oxidation number of an element occurs.

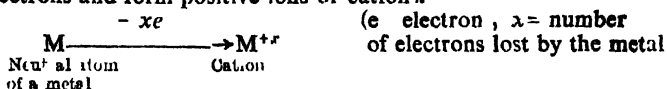
Some more oxidation reduction reactions are given here. The substances that are oxidised or reduced are also indicated.

Reaction	
$2\text{Na} + \text{H}_2 = 2\text{NaH}$	Na oxidised; H_2 reduced.
$\text{NaH} + \text{H}_2\text{O} = \text{NaOH} + \text{H}_2$	NaH .. ; H_2O ..
$3\text{Mg} + \text{N}_2 = \text{Mg}_3\text{N}_2$	Mg .. ; N_2 ..
$\text{I}_2 + \text{H}_2\text{S} = 2\text{HI} + \text{S}$	H S .. ; I ..
$\text{Zn} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2$	Zn .. ; H_2SO_4 ..
$\text{H}_2\text{S} + 2\text{FeCl}_3 = 2\text{FeCl}_2 + 2\text{HCl} + \text{S}$	H S .. ; FeCl_3 ..
$\text{C}_2\text{H}_4 + \text{Br}_2 = \text{C}_2\text{H}_4\text{Br}_2$	C_2H_4 .. ; Br_2 ..
$\text{CuCl}_2 + \text{Cu} = 2\text{CuCl}$	Cu .. ; CuCl_2 ..
$3\text{CuO} + 2\text{NH}_3 = \text{N}_2 + 3\text{H}_2\text{O} + 3\text{Cu}$	NH .. ; CuO ..
$\text{PbO}_2 + 4\text{HCl} = \text{PbCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$	HCl .. ; PbO_2 ..
$2\text{H}_2\text{S} + \text{SO}_2 = 3\text{S} + 2\text{H}_2\text{O}$	H S .. ; SO_2 ..
$\text{SO}_2 + \text{Cl}_2 + 2\text{H}_2\text{O} = 2\text{HCl} + \text{H}_2\text{SO}_4$	SO_2 .. ; Cl_2 ..
$\text{MnO} + 2\text{NaCl} = 3\text{H}_2\text{SO}_4 + \text{MnSO}_4 + 2\text{NaHSO}_4 + \text{Cl}_2 + 2\text{H}_2\text{O}$	NaCl oxidised; MnO reduced.
$\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{HI} = 7\text{H}_2\text{O} + 4\text{K}_2\text{SO}_4 + \text{Cr}(\text{SO}_4)_3 + 3\text{I}_2 + 7\text{H}_2\text{O}$	KI .. ; $\text{K}_2\text{Cr}_2\text{O}_7$..
$\text{AgCN} + \text{CN}^- \rightarrow [\text{Ag}(\text{CN})_2]^-$	CN^- .. ; AgCN ..
$\text{SnS}_2 + \text{S} \rightarrow \text{SnS}$	S^- .. ; SnS_2 ..
$\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$	NH_4^+ .. ; NO_2^- ..
$\text{Cl}_2 + \text{H}_2\text{O} = \text{HOCl} + \text{HCl}$	$(\text{NH}_4\text{NO}_2 \text{ oxidised and reduced})$
$3\text{I}_2 + 6\text{NaOH} = \text{NaIO}_3 + 5\text{NaI} + 3\text{H}_2\text{O}$	$\text{Cl}_2 \rightarrow \text{HOCl}$ (Oxidn) $\text{Cl}_2 \rightarrow \text{HCl}$ (Red)
$2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$	$\text{I}_2 \rightarrow \text{NaIO}_3$ (Oxid) $\text{I}_2 \rightarrow \text{NaI}$ (Red)
$4\text{KClO}_2 = 2\text{KClO}_4 + 2\text{KCl}$	$\text{KClO}_3 \rightarrow \text{O}_2$ (Oxid) $\text{KClO}_3 \rightarrow \text{KCl}$ (Red) $\text{KClO}_2 \rightarrow \text{KClO}_4$ (Oxid) $\text{KClO}_2 \rightarrow \text{KCl}$ (Red)

Some substances can act as both oxidising agents and reducing agents.

Substance	Reaction showing oxidising property	Reaction showing reducing property
Nitrous acid	$\Delta \text{O}_2 + \text{Br}_2 + \text{H}_2\text{O} = 2\text{HBr} + \text{HNO}_3$	$\text{SnO}_2 + 2\text{HNO}_3 = \text{H}_2\text{SnO}_3 + 2\text{NO}$
Sulphur dioxide	$\text{SO}_2 + 2\text{H}_2\text{S} = 3\text{S} + 2\text{H}_2\text{O}$	$2\text{KMnO}_4 + 5\text{SO}_2 + 2\text{H}_2\text{O} = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 2\text{H}_2\text{SO}_4$
Hydrogen peroxide	$\text{PbS} + 4\text{H}_2\text{O}_2 = \text{PbSO}_4 + 4\text{H}_2\text{O}$	$\text{Ag}_2\text{O} + \text{H}_2\text{O}_2 = 2\text{Ag} + \text{H}_2\text{O} + \text{O}_2$

Electro potential series of metals. We know that the metals (including the non metal hydrogen) tend to lose one or more electrons and form positive ions or cations.



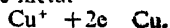
But the degree of this tendency is not the same for all the metals.

The higher the tendency to ionise the greater is the reducing power of the metal. Based on this tendency, the metals have been arranged in a series. Thus the series in which the metals are arranged in order of their decreasing tendency to give up electrons and to form positive ions is called the **electropotential series** or the **electro chemical series of the metals**.

In the electro chemical series, the most electropositive metals with stronger reducing ability are at the top while the least electro positive metals with weaker reducing power are at the bottom.

In order to get a correct idea of the principle on which the arrangement of metals in the series is based, one must clearly understand the meaning of the term **electric potential**.

When a metal is immersed in a solution containing its own ions either of the two possible but opposite reactions may take place. The neutral atoms of the metal may pass into the solution in the form of its positively charged ion by losing electrons or the ions in the solution may form the neutral atoms and deposit on the metal. For example when a zinc rod is partially immersed in a solution of zinc sulphate a minute amount of zinc is found to ionise and goes into the solution in the form of Zn^{++} ions and each zinc atom while passing in the ionic state leaves behind two electrons in the metal rod $\text{Zn} - 2e \rightarrow \text{Zn}^{++}$. Consequently the zinc becomes negatively charged relative to the solution and an electric potential is set up between the metal and the solution. The negative charge on the metal does not allow the ions to move far away from the metal. On the other hand if a rod of copper is kept in contact with a solution of copper sulphate a minute amount of copper ions is converted into copper atom and deposits on the metal rod. During the deposition each Cu^{++} ion takes up two electrons from the metal.



As a result the copper acquires a positive charge leaving the solution negatively charged. Here, also a potential difference exists between the metal and the solution. Each metal when surrounded by its own ions in solution will form a **simple electrode** which is associated with a definite electrical potential. Thus, by

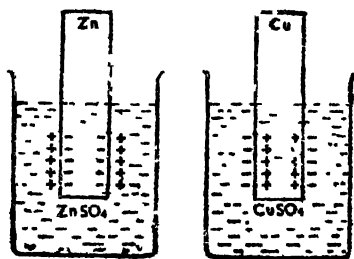


Fig. 1(28) Electrode potential which is associated with a definite electrical potential. Thus, by

immersing a metal in its normal solution (i.e. solution containing one gm-ion per litre), it is possible to compare the ionising tendency or reduction ability of different metals.

For assigning numerical values to the electrode potentials, it is necessary to choose a standard electrode and fix an arbitrary value to the potential of the same. In practice, the standard electrode used for comparison of all electrode potentials is the hydrogen electrode in which pure hydrogen gas at one atmosphere pressure is kept in contact with an acid solution containing H at unit concentration. The potential of this electrode is arbitrarily taken as zero. The electrode potentials of some familiar metals under the standard condition are shown in the adjacent table.

The standard electrode potential is a measure of the electropositive character of the metal. From the table, it is clear that the metals are arranged in the electro-

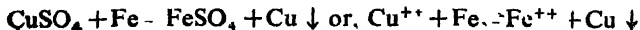
Metal	Standard electrode potential
K	- 2.92
Na	- 2.71
Ca	- 1.87
Mg	- 1.55
Al	- 1.63
Zn	- 0.758
Fe	- 0.441
Pb	- 0.13
H	0.00
Cu	+ 0.79
Ag	+ 0.799
Au	+ 1.5

chemical series in order of increasing standard electrode potentials. The greater the negative value of the potential, the greater is the tendency for a metal to ionise.

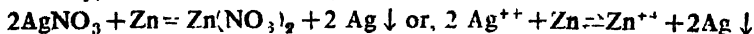
This series may be used as a guide to decide the relative chemical reactivities of the elements.

(A) Reducing action : The metal occupying the higher position in the series will have greater tendency to give up electrons and will behave as a stronger reducing agent than the metal in the lower position. Thus, aluminium is a stronger reductant than iron.

(B) Displacement reaction : A metal higher up in the series displaces a metal below it from the solution of its salts. Thus, iron displaces copper from a CuSO_4 solution. Iron occupies a higher position in the electro potential series of metals than copper and goes into the solution forming ions by loss of electrons.



Similarly, silver is displaced by zinc from a solution of silver nitrate.



The above displacement reactions are illustrated by the following experiments.

An iron nail is placed in a copper sulphate solution taken in a beaker. After some time, a red deposit of copper is found on the iron nail. The copper has been displaced from the solution by

iron which has gone into the solution forming ferrous sulphate. [Fig. 1 29]

A solution of silver nitrate of moderate concentration is taken in a beaker having a zinc rod fixed on a cork at the bottom. After some time, a beautiful tree-like growth of silver crystals is found round the rod. This is known as the silver tree [Fig. 1(30)]

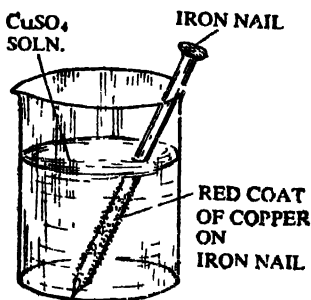


Fig 1 29 Displacement of copper by iron

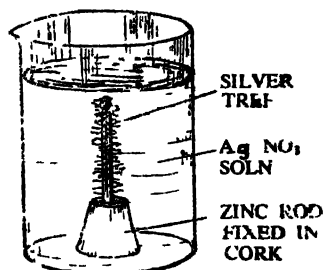


Fig 1 (30). Displacement of silver by zinc - Silver tree

The reverse reaction is never found to occur. There is no change when copper is added to ferrous sulphate solution or silver can never displace zinc from a solution of zinc nitrate.

(C) Displacement of hydrogen from water and acids: Metals above hydrogen (with the exception of lead and tin) are capable of displacing hydrogen from water. The higher the metal in the series, the more vigorous is the reaction with water. (Vide reactions of metals with water given in the Chapter 2 under. Group B of this book), Metals (below hydrogen in the series) like Cu, Hg, Ag do not react with water liberating hydrogen.

Similarly, metals preceding hydrogen (with the exception of lead) can liberate hydrogen from dil. mineral acids like dil. HCl, H₂SO₄ but the metals following hydrogen are unable to do so.

(D) Combination with oxygen and chlorine. The ease of formation, basic nature and stability of the metallic oxides (or chlorides) increase with the increasing electropositive characters of the metals. Consequently, the metal higher up in the series possesses greater tendency to combine with oxygen and chlorine to form its oxide and chloride respectively than the metal below it.

Thus sodium and potassium form stable oxides when the metals come in contact with oxygen. Magnesium, zinc, aluminium etc combine with oxygen at high temperatures.

The oxides of the metals above and upto aluminium (with the exception of magnesium) are too stable to be reduced by heated carbon or by hydrogen even at very high temperatures. The stability

of the oxides of the metals below aluminium gradually falls with the decreasing electropositeness of the metals. The oxides of the metals below aluminium are reduced to the respective metals by heated carbon. The metals like copper, silver, mercury form oxides with difficulty. The oxide of copper is reduced to the metal when heated in a current of hydrogen. The oxides of silver and mercury etc. are even decomposed to produce oxygen by heat alone. This accounts for the fact that cupric oxide, silver oxide have oxidising properties while Na_2O or K_2O does not have this property.

The affinity of metals for chlorine and the stability of metallic chlorides can similarly be explained.

NB It is to be noted that the non-metals have also been arranged according to the decreasing order of their tendencies to accept electrons i.e. decreasing order of electro-negative character.

Non metals
Fluorine
Oxygen
Chlorine
Bromine
Iodine
Sulphur
Phosphorus
Nitrogen
Carbon

From the adjacent table it is clear that chlorine is the most electronegative element with greater tendency to take up electrons than bromine or other non-metals below it. Thus, chlorine behaves as a stronger oxidising agent than bromine and iodine. Conversely a more electronegative element will displace a less electronegative element from its combination with a metal (e.g. chlorine displaces bromine from potassium bromide while bromine displaces iodine from potassium iodide).

bromine from potassium bromide while bromine displaces iodine from potassium iodide.

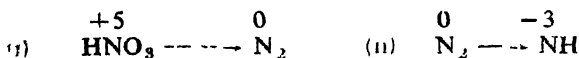


Use of oxidation number in calculating chemical equivalents.
We know that in most cases the oxidation number of an element in a particular compound is equal to the number denoting its valency. So, from the change in oxidation number of an element which takes place in a redox reaction either in the free state or in combination the equivalent weight of the element can be calculated using the following relation.

Chemical equivalent

$$= \frac{\text{Molecular weight of the element}}{\text{Total change in oxidation number of the element}}$$

It will be clear from the following conversions



In the first case, the oxidation number of nitrogen is decreased by 5 units ($+5 \rightarrow 0$)

$$\text{Equivalent weight of nitrogen} = \frac{14}{5} = 2.8$$

In the second case, nitrogen suffers a decrease of 3 units ($0 \rightarrow -3$) in oxidation number. So the equivalent weight of nitrogen

$$= \frac{14}{3} = 4.68.$$

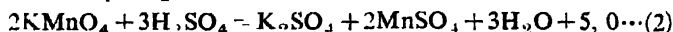
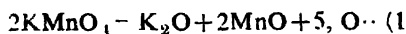
Equivalent weight of an oxidising agent and a reducing agent :

The equivalent weight of an oxidising agent is defined as the parts by weight of the substance which contains 8.00 parts by weight of available oxygen (or its equivalent).

Or reacts with 1.008 parts by weight of available hydrogen (or its equivalent)

By 'available' is meant capable of being utilised in the oxidation.

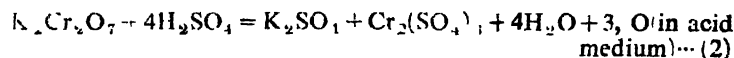
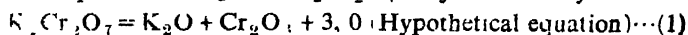
The equivalent weight of KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ may be calculated as—



From the hypothetical equation (1) or the equation (2) in acid medium, it is seen that two molecules of KMnO_4 supply 5 atoms of oxygen which may be utilised in the oxidation process

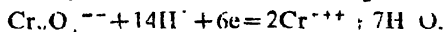
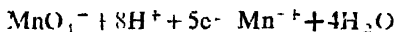
$$\begin{aligned} \text{So, equivalent weight of } \text{KMnO}_4 &= \frac{2\text{KMnO}_4}{10} \\ &= \frac{\text{Mol. wt. of } \text{KMnO}_4}{5} = \frac{158}{5} = 31.6 \end{aligned}$$

The equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7$ may be similarly determined.



$$\begin{aligned} \therefore \text{Eq. wt. of } \text{K}_2\text{Cr}_2\text{O}_7 &= \frac{\text{K}_2\text{Cr}_2\text{O}_7}{6} = \frac{\text{Mol. wt. of } \text{K}_2\text{Cr}_2\text{O}_7}{6} \\ &= 49.04 \end{aligned}$$

According to the modern concept, oxidation is a process which results in the loss of one or more electrons by atoms or ions. So, the equivalent weight of an oxidising agent is the molecular weight of the substance divided by the total number of electrons gained by the oxidising ion per molecule of the oxidant. In the acid medium, the partial ionic equations for normal reduction of KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ are as follows :



Hence, $\frac{\text{Mol. wt. of } \text{KMnO}_4}{5}$ and $\frac{\text{Mol. wt. of } \text{K}_2\text{Cr}_2\text{O}_7}{6}$ will in-

dicate the equivalent weights of KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ respectively.

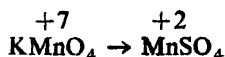
The equivalent weight of an oxidising agent may also be determined by the change of oxidation number which the reduced element suffers. It may be defined as the quantity of the oxidising

agent which involves a change of one unit in the oxidation number.

Hence, the equivalent weight of an oxidant

$$= \frac{\text{Mol. wt. of oxidant}}{\text{Total changes in oxidation state}}$$

In presence of dil. sulphuric acid, KMnO_4 is reduced to MnSO_4 , *i.e.*



Hence, the change in oxidation number of Mn is from +7 to +2 (decreased by +5 units).

\therefore Eq. wt of KMnO_4 is equal to the $\frac{1}{5}$ th of the mol. wt. of KMnO_4 .

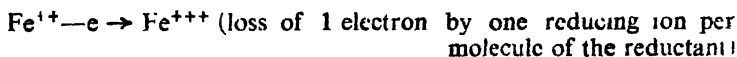
Similarly, the equivalent weight of a reducing agent may be defined as—

(i) the parts by weight of the substance which contains 1.008 parts by weight of available hydrogen (or its equivalent) or reacts with 8.00 parts by weight of oxygen (or its equivalent).

(ii) the molecular weight of the substance divided by the total number of electrons lost by each reducing ion of the reductant.

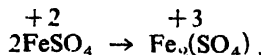
(iii) the molecular weight of the substance divided by the total change in oxidation number which one atom of the oxidised element experiences.

Let us consider the oxidation of ferrous sulphate to ferric sulphate. The partial ionic equation for this conversion is as follows :



$$\therefore \text{Eq. wt. of FeSO}_4 = \frac{\text{Mol. wt. of FeSO}_4}{1}$$

According to the concept of oxidation number, the conversion of ferrous sulphate into ferric sulphate may be depicted as follows :



Here, the change in oxidation number per atom of iron is from +2 to +3, or by one unit of oxidation.

\therefore The eq. wt of FeSO_4 is equal to its molecular weight divided by 1. So, the equivalent weight and molecular weight of a ferrous salt are identical.

CHAPTER 8

THE GAS LAWS

Characteristics of the gaseous state : We know that matter exists in three different states—solid, liquid and gaseous. Of the three states, the gaseous state has certain characteristics which distinguish it from the other two states.

A substance in the gaseous state has neither definite shape nor volume and tends to fill completely with a uniform density the available space of the container in which it is confined. When different gases which do not react chemically are brought in contact in any proportion whatsoever, they intermix almost immediately or diffuse rapidly into each other forming a homogeneous mixture. Many physical properties are found to be identical for all gases (both elementary and compound) in spite of having differences in their chemical characters.

A gas differs from a liquid or a solid in that the volume of a gas is markedly sensitive to changes of pressure and temperature. The volume change of a gas is appreciable even for a minor change in its pressure or temperature. But the change in volume of a solid or a liquid under similar situation is practically nil. Hence, to specify a quantity of a gas, it is necessary to mention its pressure and temperature.

According to Avogadro, the ultimate material particles in a gas are its molecules. It is further known that in the gaseous state, the molecules constituting the gas are far apart from one another *i.e.* the inter-molecular attraction between the molecules is very feeble. Further, the molecules of a gas are not in a state of rest but are in a state of constant or ceaseless motion in all directions with all possible velocities.

A gas is also characterised by its low density, high compressibility and high expansibility.

When the pressure on a gas is increased, the intermolecular spaces between its molecules get reduced and as a result, the density of the gas increases with simultaneous diminution in its volume.

The identity in behaviour of different gases is evident from the following facts :

(i) *All gases have the same compressibility.* Thus, when the pressure on 100 c.c. of any of the gaseous substances like air, oxygen,

hydrogen, carbondioxide is doubled (at constant temp.), the volume

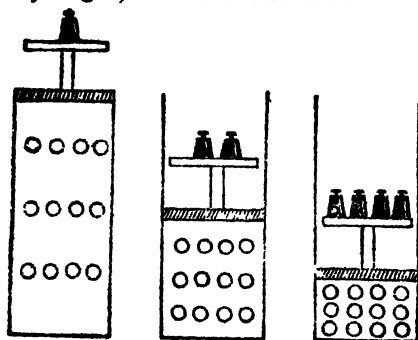


Fig. 1(31) Relation between volume and density of a gas with pressure.

of the gas reduces to 50 c.c. ; if the pressure be made four times, the volume will be 25 c.c. Similarly, the pressure being reduced, the volume increases proportionally. It is to be borne in mind that the change of pressure on a gas will bring an inevitable change in its density.

(ii) Again, all gases are found to expand or contract equally when heated or cooled to the same extent (at constant pressure). Thus, at the constant pressure, if the temperature

ture of 100 c.c. of any of the gases referred to above is raised from 0°C to 50 C. the volume of the gas will become 118.3 c.c. It has been clearly shown in the fig. 1(32) that the three different gases expand to the similar extent when heated on the water bath through the same temperature. It is also true that the gases will contract equally if the temperature is lowered to the similar extent. Hence, it may be concluded that *all gases have the same coefficient of expansion.*

The Gas Laws : The most striking fact about gases is that irrespective of their chemical nature, they obey some simple laws with regard to their physical properties. The laws or common relations regulating the pressure, volume and temperature of any gas are called the gas laws. These laws are enunciated below :

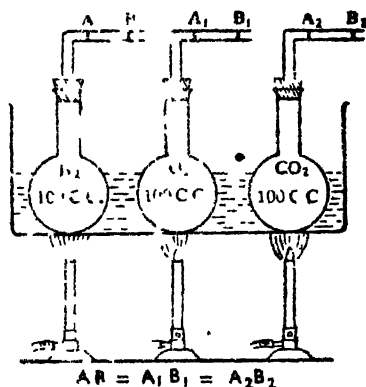


Fig. 1(32) All gases have the same coefficient of expansion.

(1) **Boyle's law :** (Pressure-volume relationship of a gas at constant temperature. Robert Boyle 1662) studied the effect of pressure on the volume of a gas at constant temperature. From the observed variation of the volume with pressure, he established a simple relation between the two and expressed the same in the form of a law known as Boyle's law. The law states :

At constant temperature, the volume of a definite mass of any gas varies inversely as the pressure on the gas.

Thus, the temperature being maintained constant, the volume of a given mass of a gas diminishes proportionately with increasing pressure or increases as the pressure decreases. If the original pressure on the gas for example, is doubled, its volume is reduced to one half and if the pressure is reduced to half, the volume is increased to double the original volume.

If P be the pressure and V the volume of a given mass of a gas, then according to Boyle's law.

$$P \propto \frac{1}{V} \text{ (the mass and temp. remaining constant)}$$

$$\text{or } V = k \frac{1}{P} \text{ (} k \text{ is a proportionality constant)}$$

or $PV = k$ (constant). This is the mathematical expression of Boyle's law. So, Boyle's law may alternatively be stated as.

At a fixed temperature, the product of the pressure and volume of a definite mass of any gas is constant.

The value of the constant k depends on the temperature and mass of the gas.

If V_1, V_2, V_3 , etc. be the volumes of a fixed quantity of a gas at constant temperature under pressures denoted respectively by P_1, P_2, P_3 , etc. then by the above law

$$P_1 V_1 = P_2 V_2 = P_3 V_3, \text{ etc.} = k \text{ constant.}$$

This means that whatever may be the magnitudes of P and V , their product will always remain the same for a fixed quantity of a gas at fixed temperature.

The relation between pressure and volume in accordance with the equation, $PV = k$ can be represented graphically by plotting the pressures as ordinates and the corresponding volumes containing a definite mass of a gas at constant temperature, as abscissae. The curve drawn through the resulting points is found to be a rectangular hyperbola (Fig. 1(33)). The nature of the graph fully proves the validity of Boyle's law. Such a curve showing the variation of volume with pressure at constant temperature, is known as *isotherm* (constant temp. plot). Since the value of the constant (k) mentioned above will change with temperature, there will be a separate curve or isotherm of exactly same nature (hyperbola) for each fixed temperature. The higher curve as shown in Fig. 1(33) corresponds to the higher temperature.

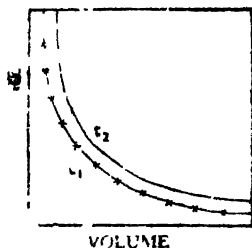


Fig. 1(33) Boyle's law isotherms $t_2 > t_1$

Effect of pressure on the density of a gas at constant temperature :

From Boyle's law, we know—

$$P_1 V_1 = P_2 V_2 \quad \text{or} \quad \frac{V_1}{V_2} = \frac{P_2}{P_1} \quad (\text{at constant temp.})$$

Now, let us suppose that a given mass (M) of a gas has the volume V_1 and density D_1 under a pressure P_1 and a volume V_2 and density D_2 under a pressure P_2 .

$$\text{Then, } D_1 = \frac{M}{V_1} \text{ and } D_2 = \frac{M}{V_2} \text{ or } \frac{V_1}{V_2} = \frac{D_2}{D_1}$$

i.e. the density of a gas at a given temperature is inversely proportional to its volume.

$$\therefore \frac{V_1}{V_2} = \frac{P_2}{P_1} = \frac{D_2}{D_1}$$

$$\therefore \frac{D_2}{D_1} = \frac{P_2}{P_1} \text{ or } \frac{D_1}{D_2} = \frac{P_1}{P_2} = k \text{ (constant)}$$

$$\therefore \frac{P}{D} = k \therefore P = kD \text{ or } P \propto D$$

This relation may be expressed in the form of a law as—

Temperature remaining constant, the density of a gas varies directly as the pressure to which the gas is subjected. This may be regarded as a corollary of Boyle's law

Charles' law. The variation of the volume of a given mass of a gas with temperature at constant pressure was investigated by Charles and he expressed it in the form of a law (1787) known as Charles' law. Gay Lussac in 1802 obtained the similar results independently. Charles' law may be stated as,

At constant pressure, the volume of a given mass of any gas increases (or diminishes) by $\frac{1}{273}$ of its volume at 0°C for each 1°C rise (or fall) in temperature.

This constant fraction (i.e. $\frac{1}{273}$) is the coefficient of expansion (or contraction) of all gases irrespective of their chemical nature
(A more precise value of this fraction is $\frac{1}{273.16}$)

Let V_0 be the volume (in c.c.) of a definite mass of a gas at 0°C (pressure being kept constant), then

$$\begin{aligned} \text{the vol. due to } 1^\circ\text{C increase in temp. will become } & V_0 + \frac{V_0}{273} \\ & = V_0 \left(1 + \frac{1}{273} \right) \text{ c.c.} \end{aligned}$$

$$\begin{aligned} \text{" " " " } 10^\circ\text{C} \text{ " " " " " " } & V_0 + \frac{V_0 \times 10}{273} \\ & = V_0 \left(1 + \frac{10}{273} \right) \text{ c.c.} \end{aligned}$$

$$\begin{aligned} \text{" " " " } t^\circ\text{C} \text{ " " " " " " } & V_0 + \frac{V_0 \times t}{273} \\ & = V_0 \left(1 + \frac{t}{273} \right) \text{ c.c.} \end{aligned}$$

In the similar way,

$$\begin{aligned} \text{The vol. due to } 1^{\circ}\text{C decrease in tempr. will become } V_0 - \frac{V_0}{273} \\ = V_0 \left(1 - \frac{1}{273}\right) \text{ c.c.} \\ \text{,, ,, ,, ,, } 10^{\circ}\text{C} \text{ ,, ,, ,, ,, ,, } V_0 - \frac{V_0 \times 10}{273} \\ = V_0 \left(1 - \frac{10}{273}\right) \text{ c.c.} \\ \text{,, ,, ,, ,, } t^{\circ}\text{C} \text{ ,, ,, ,, ,, ,, } V_0 - \frac{V_0 \times t}{273} \\ = V_0 \left(1 - \frac{t}{273}\right) \text{ c.c.} \end{aligned}$$

Absolute zero and Absolute temperature: From above, it is obvious that if the temperature of the gas be lowered to -273°C then according to Charles law, the volume occupied by a gas at 0°C under a const pressure) will become

$$V_0 - \frac{V_0 \times 273}{273} \text{ c.c. } V_t \left(1 - \frac{273}{273}\right) = 0 \text{ c.c.}$$

That is to say that at -273°C , a gas occupies no volume. Temperature at which volume of a gas vanishes or represents the ultimate thermal contraction of the gas is known as *absolute zero*. A temperature lower than absolute zero (i.e. -273°C) can never be conceived of. This is purely hypothetical. Attainment of such a low temperature has never been possible in practice, for usually long before -273°C is approached, a gas liquefies or even solidifies. However from this theoretical approach, a new temperature scale in which the zero is at -273° but each degree has the same magnitude as the centigrade degree has been devised and it is called the *absolute scale of temperature*. The temperatures on this scale are said to be *absolute temperatures* and are expressed in 'A (absolute) or 'K *(degrees Kelvin) after the name of Lord Kelvin who was the first scientist to conceive of the existence

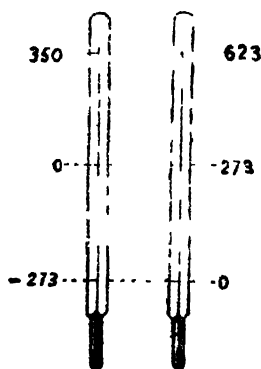


Fig. 1(94) Centigrade and Kelvin scales of temperature

* The term centigrade has now been replaced by Celsius who is the inventor of the centigrade scale of temperature.

** Following the international recommendation, the sign of degree is not used before Kelvin. So, in place of $T^{\circ}\text{K}$, only TK is written.

of the absolute zero state. Any temperature T on the new scale is obtained by adding 273 to the centigrade temperature t .

$$T = t + 273$$

Thus, $0^\circ\text{C} = 273^\circ\text{A}$ or 273°K

$$10^\circ\text{C} = 10 + 273 \text{ or } 283^\circ\text{A}$$

$$100^\circ\text{C} = 100 + 273 \text{ or } 373^\circ\text{A}$$

$$-10^\circ\text{C} = (-10 + 273) \text{ or } 263^\circ\text{A}$$

$$-273^\circ\text{C} = (-273 + 273) \text{ or } 0^\circ\text{A}$$

The freezing and boiling points of water on the absolute scale are 273°A and 373°A respectively.

Expression of Charles' law in terms of absolute temperatures :
If the volumes of a given mass of a gas are designated by V_0 , V_1 and V_2 at 0°C , $t_1^\circ\text{C}$ and $t_2^\circ\text{C}$ respectively, (at constant pressure),

$$\begin{aligned} \text{then according to Charles' law } V_1 &= V_0 + V_0 \frac{t_1}{273} = V_0 \left(1 + \frac{t_1}{273}\right) \\ &= V_0 \left(\frac{273 + t_1}{273}\right) \end{aligned}$$

$$V_2 = V_0 + V_0 \frac{t_2}{273} = V_0 \left(1 + \frac{t_2}{273}\right) = V_0 \left(\frac{273 + t_2}{273}\right)$$

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \text{ or } \frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V}{T} = \text{K constant}$$

or, $V \propto T$ so long as the pressure remains constant and here T_1, T_2, T are the temperatures on the absolute scale. This is the mathematical expression of Charles' law which may alternatively be stated as,

At definite pressure the volume of a given mass of any gas is directly proportional to its absolute temperature.

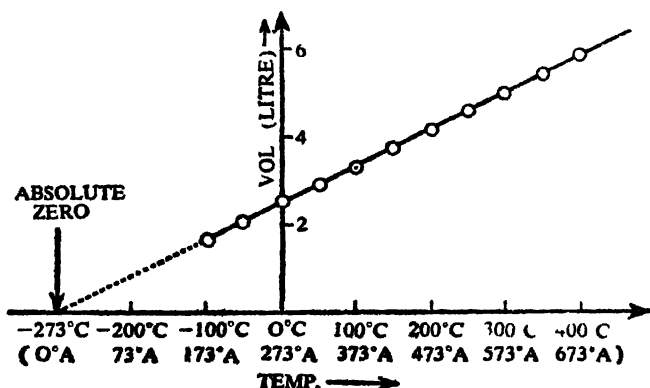


Fig. 1(85) Graphical representation of Charles' law

That is to say, if pressure be kept unaltered, the volume of a given quantity of a gas increases or decreases proportionally with the increase or decrease of temperature on the absolute scale.

If the volumes of a gas are plotted against temperatures (at a fixed pressure), a straight line meeting the X-axis at -273°C is obtained. Fig. 1(35)] This has been found to be true for almost all gases. This proves the validity of Charles' law

The variation of the pressure of a gas with temperature at constant volume is expressed by the generalisation often called Gay Lusaac's law. This law is stated as

"If the volume of a definite mass of a gas be kept constant, its pressure varies directly as the absolute temperature.

$P \propto T$ where V is constant.

Thus,

$\frac{P_1}{P_2} = \frac{T_1}{T_2}$ (P_1 is the initial pressure at the tempr. T_1 and P the pressure when tempr. is changed to T_2 ; temperatures being measured at absolute scale)

It has already been shown that Charles' law can be graphically represented by a straight line. By plotting the volumes against absolute temperatures at selected pressures, we obtain different straight lines one for each constant pressure. These lines are called isobars (iso = same bar = pressure) which on extrapolation converge to zero volume. It may further be noted that the slope of an isobar is greater when then the pressure is lower [Fig. 1(36)].

Similarly, linear graphs are obtained when pressures are plotted against absolute temperatures (volume being kept constant) [Fig. 1(37)]

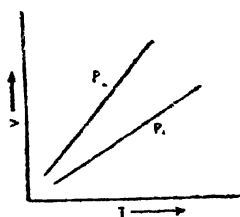


Fig. 1(36) Isobars ($P_1 > P_2$)

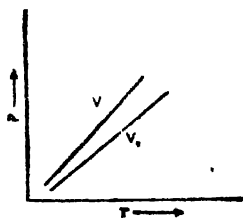


Fig. 1(37) Graphs of P vs. T at const. volume

Relationship between the density (D) and absolute temperature (T)

It can be proved that at constant pressure, the density of a given mass of any gas is inversely proportional to the absolute temperature. This may be regarded as the corollary to Charles' law.

According to Charles' law, $\frac{V_1}{T_1} = \frac{V_2}{T_2}$; or $\frac{V_1}{V_2} = \frac{T_1}{T_2}$.

We know that $M = V_1 D_1 = V_2 D_2$ (M or mass remaining constant)

$$\text{or, } \frac{V_1}{V_2} = \frac{D_2}{D_1}; \text{ so } \frac{V_1}{V_2} = \frac{T_1}{T_2} = \frac{D_2}{D_1} \quad \text{or} \quad \frac{D_2}{D_1} = \frac{T_1}{T_2}$$

$$\text{or, } T_1 D_1 = T_2 D_2 = \text{etc} = DT = K \text{ (constant)}$$

$$\therefore D = \frac{K}{T} \quad \therefore D \propto \frac{1}{T}$$

Equation of state—combination of Boyle's and Charles' laws
(Combined effect of temperature and pressure on the volume of a gas): Boyle's law and Charles' law may be combined in the form of a single equation which represents the relation between temperature, pressure and volume of a given mass of a gas. Such an equation is described as an equation of state.

Let V be the volume of a given mass of a gas at pressure P and temperature T (absolute). Now,

$$V \propto \frac{1}{P} \text{ when } T \text{ remains constant (Boyle's law)}$$

and $V \propto T$ when P remains constant (Charles' law)

$\therefore V \propto \frac{T}{P}$ when both T and P vary (combination of Boyle's and Charles' laws)

$$\text{or } \frac{PV}{T} = K = \text{Constant or } PV = KT,$$

It follows that the product of the pressure and volume of a given quantity of a gas varies directly as the absolute temperature. This equation of state implies that for a given quantity of a gas, the simultaneous change of pressure and temperature will cause an adjustment of volume so that the quantity $\frac{PV}{T}$ remains unaltered

Similarly, it can be proved that

$$\frac{PV}{T} = \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \dots = \frac{P_n V_n}{T_n} = K \quad [\text{If } P_1, V_1; P_2, V_2, \dots]$$

$\dots P_n, V_n$ etc. be the pressures and volumes of the same mass of gas at temperature T_1, T_2, \dots, T_n (absolute) respectively.

The equation of state can also be established alternatively without the application of the law of variation.

Let us suppose that the gas has initially a volume V_1 at the pressure P_1 and temperature T_1 ; then when the pressure and temperature are changed to P_2 and T_2 respectively, the volume will be V_2 .

Now, if the pressure is altered from P_1 to P_2 , maintaining the temperature at T_1 , and if the accompanying volume change is from V_1 to V_1' , then according to Boyle's law, we get

$$P_1 V_1 = P_2 V_1' \quad \text{or} \quad V_1' = \frac{P_1 V_1}{P_2}$$

If the pressure is now kept constant at P_2 and the temperature is changed from T_1 to T_2 , the volume will then change from V_1' to V_2 . It follows from Charles law that,

$$\frac{V_1'}{T_1} = \frac{V_2}{T_2}$$

Inserting the value of V_1' , we arrive at

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{i. e.} \quad \frac{P_1 V_1}{T_1} = \text{a constant} = K \quad \text{or} \quad PV = KT.$$

In the equation $PV = KT$, K is a constant. Its value depends upon the mass of the gas taken as the amount of any gas is proportional to its volume under a given condition of temperature and pressure. It is known from Avogadro's law that one gram-molecule of any gas occupies the same volume at a given temperature and pressure. So if one mole is considered and P and T are the same, V will obviously be the same for all gases

The proportionality constant K in equation $PV = KT$ will have the same value for a gram-molecule of all gases under all physical conditions. When the mass of a gas is one mole, the constant K is known as the **molar gas constant** and is denoted by the symbol R . Hence the gas law equation for one mole of a gas is expressed as $PV = RT$. R is also referred to as the **Universal gas constant** as its value is the same for all gases irrespective of their chemical nature. For n moles of a gas, the above equation becomes

$$PV = nRT,$$

Again, the same equation can be obtained by the combination of Boyle's law, Charles' law and Avogadro's law.

According to Boyle's law $V \propto \frac{1}{P}$ (when n i.e. number of moles and T are constant)

„ „ Charles' law $V \propto T$ (when n and P are constant)

and „ „ Avogadro's law $V \propto n$ (when P and T are constant,

$$\therefore V \propto \frac{nT}{P} \quad (\text{when } n, P \text{ and } T \text{ vary})$$

$$\text{or} \quad V = \frac{RnT}{P}, [R = \text{constant}]$$

$$\therefore PV = nRT.$$

It should be noted here that Boyle's law, Charles' law and Avogadro's law can together be applied to determine the molecular weight of a gaseous substance.

We know that for n moles of a gas, the equation of state assumes the form $PV = nRT$.

If w and M be the mass and molecular weight of the gas respectively, then

$$n = \frac{w}{M}$$

$$\therefore PV = \frac{w}{M} RT$$

$$\therefore M = \frac{wRT}{PV}$$

From the above discussions, the alternative forms of the equation of state of any gas are listed below :

- (i) $PV = RT$ (for one mole of a gas)
- (ii) $PV = nRT$ (for any quantity of a gas i.e. n moles)
- (iii) $PV = \frac{w}{M} RT$ (for w gms of molecular wt M).

The gases which strictly obey the laws of Boyle and Charles, as expressed in the form of the equation $PV = RT$ or $PV = nRT$ are known as the ideal or perfect gases and the equation stated above is known as the ideal gas equation. On the other hand, the gases which do not obey the above laws exactly are called the real or non-ideal gases. They obey these laws only at low pressures and relatively low temperatures. In fact, ideal gas is an hypothetical gas as there is no gas which follows the gas laws strictly. For an ideal gas obeying Boyle's law, the graph of pressure volume product (PV) of a gas against pressure at const. T will be represented by a straight line horizontal to the X-axis.

Similarly, the graph of PV against V at const. T will also be a straight line parallel to the X-axis.

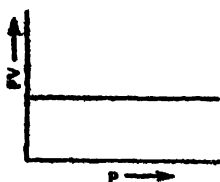


FIG. 1 (3A)

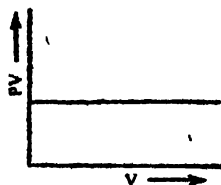


FIG. 1 (3B)

Relationship between the temperature, pressure and density of a certain quantity of gas : According to Boyle's and Charles' laws for

a definite mass of a gas, $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \text{constant}$. Here, the mass

is constant. By definition, $V_1 = \frac{M}{D_1}$ and $V_2 = \frac{M}{D_2}$ (where M = mass of the gas ; D_1 = density at pressure P_1 and absolute temp. T_1 , D_2 = density at P_2 and T_2)

$$\frac{P_1 M}{T_1 D_1} = \frac{P_2 M}{T_2 D_2} \quad \text{or,} \quad \frac{P_1}{T_1 D_1} = \frac{P_2}{T_2 D_2} = \text{constant}$$

This equation expresses the relation between the density, pressure and temperature of a given mass of a gas

Relation between absolute temperature and pressure at constant volume of gas :

We have seen that for a certain mass of a gas $PV = K = \text{constant}$. $P = \frac{K}{V} T$.

Now, if V be kept constant, then $\frac{K}{V}$ is also constant

$$\therefore P \propto T$$

This mathematical relation can be expressed in the form of the following statement -

The volume of a definite mass of a gas remaining constant, its pressure varies directly as the absolute temperature.

The above equation may be applied for indirect determination of temperature from the increase or decrease of pressure. This principle finds its application in the construction of gas-thermometers.

Numerical value of the gas constant 'R'

We know that the most general equation for 1 gram molecule of a gas is given by

$$PV = RT \quad \text{or} \quad R = \frac{PV}{T}$$

Now, P Pressure = $\frac{\text{Force}}{\text{area}}$, V Volume = Length³ and

Area = (Length)²

$$R = \frac{\text{Force}}{(\text{Length})^2} \times \frac{\text{Length}^3}{\text{Degrees}} = \frac{\text{Force} \times \text{Length}}{\text{Degrees}} = \frac{\text{work (i.e. energy)}}{\text{Degrees}}$$

R has the dimensions of energy per degree per mole i.e. energy degree⁻¹ mole⁻¹. Energy may be expressed in different units and hence the numerical value of R will vary in different systems of units. Thus, the gas constant is not an abstract number and is dependent on the units employed for stating energy.

(a) Evaluation of R in Litre-Atmosphere :

It is known that 1 gm-molecule of any gas at standard conditions of temperature and pressure *i.e.*, at 0°C (or 273°A) and 1 atm pressure occupies a volume of 22.4 litres. By expressing the volume in litres and the pressure in atmospheres, we get

$$R = \frac{PV}{T} = \frac{1 \times 22.4}{273} = 0.082 \text{ litre atmosphere per degree absolute per mole.}$$

R in other units : (b) In C. G. S. unit, P (pressure) is expressed in dynes per square centimeter, V (volume) in cubic centimeter (c.c.) and T in $^{\circ}\text{A}$. A pressure of 1 atmosphere means a weight of a column of mercury 76 cm high and 1 cm^2 in cross section at 0°C . Again, the density of mercury at 0°C is 13.6 gms/c.c and acceleration due to gravity (g) = 981 cm/sec^2 . It follows that 1 atmosphere pressure = $76 \times 13.6 \times 981 \text{ dynes/cm}^2$

Vol. of 1 mole of a gas at N.T.P. = 22400 c.c. 'cm³'

By inserting the values of P, V and T in

$$\begin{aligned} R &= \frac{PV}{T} = \frac{76 \times 13.6 \times 981 \text{ dynes/cm}^2 \times 22400 \text{ cm}^3}{273^{\circ}\text{A}} \\ &= \frac{76 \times 13.6 \times 981 \times 22400}{273} \text{ ergs per degree per mole.} \\ &= 8.315 \times 10^7 \text{ ergs degree}^{-1} \text{ mole}^{-1} \end{aligned}$$

(c) We know, $10^7 \text{ ergs} = 1 \text{ Joule}$.

$\therefore R = 8.315 \text{ joules per degree per mole.}$

Again, $4.184 \text{ Joules or } 4.184 \times 10^7 \text{ ergs} = 1 \text{ calorie}$

$\therefore R = \frac{8.315}{4.184} = 1.987 \approx 2 \text{ calories per degree per mole}$

Partial pressure and Dalton's law of partial pressures :

When different gases that do not react chemically with each other are introduced into the same container, they intermix rapidly and exert a definite pressure. Again, each of the gases in the mixture exerts its own individual pressure as if it has separately occupied the total volume of the container at the same temperature.

J. Dalton (1801) established the relation between the total pressure of a mixture of different gases and the individual pressures of the constituent gases and expressed the same in the form of a law known as Dalton's law of partial pressures. The law states :

At constant temperature, the total pressure exerted by a mixture of two or more non-reacting gases and vapours occupying a definite

volume is equal to the sum of the partial pressure of each of the constituent gases and vapours.

The partial pressure of a constituent gas or vapour in a mixture is defined as the pressure it would exert if it alone had occupied the entire volume of the vessel in which the mixture is enclosed (at the same temp.)

If P be the total pressure of a mixture of different non-reacting gases present in a closed space at a given temperature T and p_1, p_2, p_3, \dots etc. be the partial pressures (at the same temp.) of the individual constituent gases, then

$P = p_1 + p_2 + p_3 + \dots$. This is the mathematical expression of Dalton's law of partial pressures.

The concept of partial pressures is best explained by the following example. Three 1-litre flasks are filled respectively with oxygen at 200 mm pressure of Hg, nitrogen at 300 mm. and carbondioxide at 75 mm. (all at the same temperature). All the three gases are then forced into a fourth flask of 1-litre capacity. Now, according to Dalton's law, the total pressure (P) within the fourth flask is given by

$$P = p_{O_2} + p_{N_2} + p_{CO_2} = 200 + 300 + 75 = 575 \text{ mm. Hg}$$

(Where $p_{O_2}, p_{N_2}, p_{CO_2}$ denote the partial pressures of oxygen, nitrogen and carbon dioxide respectively.)

Mathematical deduction : At constant temperature, let a gas (A) occupying the volume V under pressure P_1 be mixed with another gas (B) that occupies the volume V_2 under pressure P_2 .

\therefore Total volume of the gas mixture $= V_1 + V_2$ (say V)

And let the total pressure exerted by the mixture be P and the partial pressures of the two components of the mixture be p_1 and p_2 respectively.

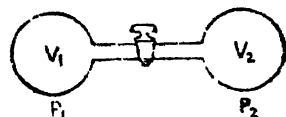


Fig. 1(88)

Due to mixing, the volume of the gas (A) changes to $(V_1 + V_2)$ under its partial pressure p_1 and the volume of the gas B also becomes $V_1 + V_2$ under its partial pressure p_2 .

Now, by applying Boyle's law, we get

$$p_1 V = P_1 V_1 \text{ and } p_2 V = P_2 V_2$$

$$\therefore p_1 = \frac{P_1 V_1}{V} = P_1 \frac{V_1}{V_1 + V_2} \text{ and } p_2 = \frac{P_2 V_2}{V} = P_2 \frac{V_2}{V_1 + V_2}$$

According to law of partial pressures (Dalton).

$$P = p_1 + p_2$$

$$\text{or, } P = \frac{P_1 V_1}{V_1 + V_2} + \frac{P_2 V_2}{V_1 + V_2}$$

$$P = \frac{P_1 V_1 + P_2 V_2}{V_1 + V_2}$$

This is the relationship between the total pressure of a gas mixture and the individual pressures of the gases constituting the mixture.

Pressure of gases collected over water : Gases collected over water are obviously moist and are saturated with water vapour (or aqueous tension) at the experimental temperature. During the collection of a gas the levels of water inside and outside the jar are kept the same as under such conditions, the total pressure of the moist gas inside the jar becomes equal to the atmospheric pressure.

According to Dalton's law of partial pressures.

pressure of the collected gas (p) + pressure of aqueous vapour at the temp^r of the experiment (f) = atmospheric pressure (P) = pressure due to the moist gas

$$\therefore p + f = P \quad \text{or, } p = P - f$$

\therefore Pressure of the dry gas = atmospheric pressure — aqueous vapour at the experimental temp^r.

So, the actual pressure of a gas collected over water is determined by subtracting the aqueous tension at the temperature of measurement from the observed pressure of the moist gas. Aqueous tensions at different temperatures may be known from Regnault's table.

Relationship between the partial pressures and the mole fractions :

Let us consider that a vessel of volume v contains a mixture of different gases at temp^r t the amounts being equal to n_1, n_2, n_3 , etc, moles respectively. Now, the equation of state which is independent of the nature of the gas can be written for each of the gases separately occupying the total volume v of the vessel.

$$p_1 v = n_1 R T \quad \text{(i)}$$

$$p_2 v = n_2 R T \quad \text{(ii)}$$

$$p_3 v = n_3 R T \quad \text{(iii) etc. } (p_1, p_2, p_3 \text{ are the partial pressures of the different gases present in the mixture.})$$

$$\therefore (p_1 + p_2 + p_3 + \dots) v = (n_1 + n_2 + n_3 + \dots) R T \quad \text{(iv)}$$

Hence, according to Dalton's law of partial pressures,

$$P v = (n_1 + n_2 + n_3 + \dots) R T = n R T \quad \text{(v)}$$

[Where P is the total pressure of the mixture ;

$n = n_1 + n_2 + n_3 + \dots$ = total number of mole in the mixture.]

On combining the equations (i), (ii) and (iii) with (v), it is found that

$$p_1 = \frac{n_1}{n} P \dots (vi); \quad p_2 = \frac{n_2}{n} P \dots (vii); \quad p_3 = \frac{n_3}{n} P \dots (viii) \text{ etc.}$$

The fractions $\frac{n_1}{n}$, $\frac{n_2}{n}$, $\frac{n_3}{n}$ etc. are known as the mole fractions of the respective gases. The mole fraction of any constituent of a mixture of gases (including solids and liquids) represents the number of moles (or molecules) of the constituent in the mixture divided by the total number of moles (or molecules) of all gases present. If the mole fractions are replaced by the respective symbols x_1 , x_2 , x_3 , ... etc, the equations (vi), (vii) and (viii) become

$$p_1 = x_1 P, \quad p_2 = x_2 P; \quad p_3 = x_3 P \text{ etc.}$$

Therefore, the partial pressure of any constituent in a mixture can be obtained on multiplication of the total pressure of the gas mixture by the mole fraction of that constituent. This expression relating the partial pressure of a gas to the total pressure of the mixture is very useful in physical chemistry.

$$\text{Again, } x_1 = \frac{n_1}{n_1 + n_2 + n_3 + \dots}; \quad x_2 = \frac{n_2}{n_1 + n_2 + n_3 + \dots}$$

$$\text{and } x_3 = \frac{n_3}{n_1 + n_2 + n_3 + \dots}$$

\therefore The sum of the mole fractions of all gases present in a mixture must be equal to unity, i.e.,

$$x_1 + x_2 + x_3 + \dots = 1.$$

Gaseous diffusion. If a bottle of ammonia is opened or some sulphuretted hydrogen gas is allowed to escape from a Kipp's apparatus in one corner of a room, the presence of either of the gases may, owing to their characteristic odours, be detected within a short time in every part of the room. This means that in spite of the room being full of air, each of the gases has a penetrating effect and mixes rapidly with the air uniformly.

Thus, when two or more gases which do not react chemically are brought in contact, they intermix with one another spontaneously to produce a homogeneous mixture. This phenomenon is a common characteristic of all gases irrespective of their densities and the process goes on even against the direction of gravity. The **natural phenomenon by virtue of which one gas is uniformly distributed into another is called the gaseous diffusion.**

This term also includes the passage of a gas through a porous wall, say of unglazed earthen ware or porcelain

Experiments to illustrate the phenomenon of diffusion :

(A) Dalton's experiment : Dalton (1801) connected by a narrow long vertical tube a bottle filled with hydrogen and another filled with carbon dioxide. The bottle containing hydrogen, the lighter gas, was kept above [as in Fig. 1(39)]. After several hours, the contents of the bottles were analysed and it was found that the gases had uniformly mixed in both the bottles. The mixing took place in opposition to gravity since the heavier gas carbon dioxide moved upward and the lighter gas hydrogen moved downward.



Fig. 1(39) Dalton's expt. on gaseous diffusion

That the phenomenon of diffusion is independent of gravity can also be proved easily by the following experiment.

If a jar of oxygen is inverted over a jar of chlorine mouth to mouth, the two gases are found to spread throughout the available space within a few minutes and the contents of the two jars appear uniformly greenish yellow in colour. Here chlorine, the heavier gas, passes upward (*i.e.* in opposition to gravity) and oxygen, the lighter one, moves downward (*i.e.* in the direction of gravity).

Graham's law of diffusion : Graham established a quantitative relation between the rate of diffusion and the relative density of a gas and expressed it in the form of a law known as Graham's law of diffusion. The law is enunciated as,

"At constant temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their densities."

The rate of diffusion means the volume of the gas diffusing per unit time. If V ml of a gas diffuse out in t seconds, then the rate of diffusion of the gas per second is $\frac{V}{t}$ ml

$$\text{i.e. Rate of diffusion} = \frac{\text{vol. of the diffused gas (in ml)}}{\text{time taken (in seconds)}}$$

It is to be kept in mind that the rate of diffusion increases with increasing temperature and pressure

Thus, while comparing the rates of diffusion, the gases must be under the identical conditions of temperature and pressure.

Mathematical expression of Graham's law : If r and d be the rate of diffusion and density of a gas respectively, then under any specified temperature and pressure.

different densities can be employed in the separation of the constituents of a gas mixture. This process of separation of gases is called *atomolysis* or pressure analysis. This method has also been applied in the separation of isotopes.

(2) The results of Graham's law of diffusion enable us to determine the molecular weight of a gas by comparing its time of effusion through a given small hole in a thin metal plate with that of a gas of known molecular weight.

(3) We know that marsh gas (methane) causes devastating fire and violent explosion in the coal mines. The electric bell (marsh gas detector) used for giving an alarm signal indicating the presense of marsh gas in mines is based on the phenomenon of diffusion. The apparatus has a porous pot connected by means of a long glass tube and a rubber stopper with one limb of a glass U-tube containing mercury. Two limbs of the tube are provided with two platinum wires, one of which is in touch with mercury and the other is just above it. Two platinum wires are connected with the terminals of a battery through an electric bell. A jar is kept inverted over the porous pot. Marsh gas being lighter than air will diffuse more quickly into the porous pot and push the mercury level up to touch the other platinum wire. As a result, the electric circuit is completed and the bell starts to ring indicating danger.

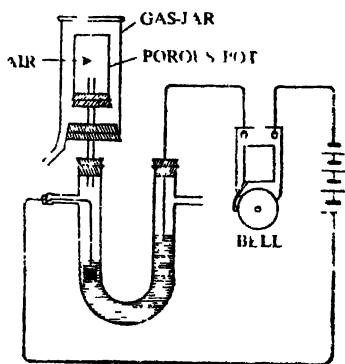


Fig. 1(41) Marsh gas detector

NOTE (1) In fact, the phenomenon of diffusion is a spontaneous tendency of any substance, gaseous, liquid or even solid to spread uniformly throughout the space available to it. But the diffusion of gases is a rapid process. In this chapter, we have confined our discussions on the gaseous diffusion only.

(2) The process of diffusion can be satisfactorily explained on the basis of the fact that the molecules of a gas are not in a state of rest but are moving in all directions with all possible velocities. The molecules of a substance in its gaseous state are far apart from each other and consequently there are large empty spaces between them. When different gases are brought in contact the molecules of each of the gases due to their perpetual random motion pass through these empty spaces and intermix together so that a uniform mixture results. This is the mechanism of the process of diffusion.

Sometimes, a gas contained in a closed vessel is found to come out gradually. A gas balloon filled with hydrogen collapses after a short time. This happens because the wall of such a gas container in spite of being made of the solid substance has porosity. There are intermolecular spaces between the molecules constituting the wall. As a result, molecules of the gas can penetrate through these spaces and pass out.

Of course, it is to be borne in mind that the rate of passing out of a gas through a wall will depend on the density of the gas as well as on the substance by which the wall is made.

(5) The density of oxygen is 16 and that of nitrogen is 14 at 0°C and 760 mm. At what temperature will oxygen have the same density as nitrogen at 0°C , assuming that the pressure remains constant?

From Charles's law, we have the relation

$$D_1 T_1 = D_2 T_2$$

Here, $D_1 = 16$, $D_2 = 14$

$$T_1 = 0^{\circ}\text{C} = 273^{\circ}\text{A}, T_2 = ?$$

$$\therefore 16 \times 273 = 14 \times T_2 \quad \text{or} \quad T_2 = \frac{16 \times 273}{14} = 312^{\circ}\text{A} \quad \text{or} \quad 39^{\circ}\text{C}.$$

(6) A certain quantity of a gas occupies a volume of 1000 ml. at 760 mm. and 27°C . Find the volume of the gas if the pressure and temperature are 1520 mm. and 327°C .

By combining Boyle's law and Charles' law, we get the gas equation $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

At the initial conditions

$$P_1 = 760 \text{ mm} \quad V_1 = 1000 \text{ ml}, \quad T_1 = 273 + 27 = 300^{\circ}\text{A}$$

At the changed conditions,

$$P_2 = 1520 \text{ mm}, \quad V_2 = ? \quad T_2 = 273 + 327 = 600^{\circ}\text{A}.$$

$$\therefore \frac{760 \times 1000}{300} = \frac{1520 \times V_2}{600} \quad \text{or} \quad V_2 = \frac{760 \times 1000 \times 600}{300 \times 1520} = 1000 \text{ ml}.$$

(7) The weight of 2.096 litres of nitrous oxide is 3.93 gms. at 17°C and 770 mm pressure. Calculate the weight of 500 ml of the gas at N.T.P.

Let V_1 be the volume of the gas at N.T.P.

$$\text{From the relation} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_1 = 760 \text{ mm}$$

$$V_1 = ?$$

$$T_1 = 273^{\circ}\text{A}$$

$$P_2 = 770 \text{ mm}$$

$$V_2 = 2096 \text{ ml}$$

$$T_2 = (273 + 17)^{\circ}\text{A}$$

$$\therefore \frac{760 \times V_1}{273} = \frac{770 \times 2096}{290} \quad \text{or,} \quad V_1 = \frac{770 \times 2096 \times 273}{290 \times 760} = 1999.1 \text{ ml}.$$

$$\therefore \text{wt. of } 1999.1 \text{ ml of the gas at N. T. P. is } 3.93 \text{ gms.}$$

$$\therefore \text{ " " } 500 \text{ " " " " " " " " } \frac{3.93 \times 500}{1999.1}$$

$$\text{or } 0.9829 \text{ gm.}$$

(8) Spherical balloons, each of 21 cm diameter, are to be filled up with hydrogen at N. T. P. from a cylinder containing the gas at 100 atmospheres and 27°C. If the cylinder can hold 2.82 litres of water, calculate the number of balloons that can be filled up.

$$\text{Volume of a balloon} = \frac{4}{3}\pi r^3 \text{ cm}^3 = \frac{4}{3} \times \frac{22}{7} \times 10.5^3 \text{ cm}^3 \quad [\because r = \frac{21}{2}]$$

$$= 4852 \text{ cm}^3 = 4.852 \text{ litres.}$$

The cylinder can hold 2.82 litres of water. This means that the volume of the cylinder is 2.82 litres and the vol. of hydrogen is 2.82 litres.

Let V_1 be the volume of the gas at N.T.P.

$$\text{From the relation } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_1 = ?$$

$$P_1 = 1 \text{ atm.}$$

$$T_1 = 273 \text{ A}$$

$$V_2 = 2.82 \text{ litres}$$

$$P_2 = 100 \text{ atmospheres}$$

$$T_2 = 273 + 27 \text{ or } 300^\circ \text{A.}$$

$$\frac{1 \times V_1}{273} = \frac{2.82 \times 100}{300} \quad \text{or} \quad V_1 = \frac{2.82 \times 100 \times 273}{300} \quad \text{or } 256.62 \text{ litres}$$

$$\therefore \text{Number of balloons required} = \frac{256.62}{4.852} = 52 \text{ (approx).}$$

(9) 1 gm-molecule of oxygen occupies a volume of 22400 ml under a pressure of 760 mm. What is the temperature of the gas in °C? ($R = 0.082 \text{ litre-atm mole}^{-1} \text{ degree}^{-1}$)

$$\text{For a gm-molecule of a gas } PV = RT \quad \therefore T = \frac{PV}{R}$$

$$\text{Here, } P = 760 \text{ mm} = 1 \text{ atm}; V = 22400 \text{ ml} = 22.4 \text{ litres}$$

$$\therefore T = \frac{1 \times 22.4}{0.082} \text{ or } 273.2^\circ \text{A}$$

$$273.2^\circ \text{A} = 0^\circ \text{C (correctly } 0^\circ \text{C} = 273.2^\circ \text{A)}$$

(10) Find out the volume of 6 gms of hydrogen at 273°C and 1.5 atmospheres.

The desired volume can be obtained by applying the relation $PV = nRT$.

From the data given,

$$P = 1.5 \text{ atm.}; n = \frac{g}{M} = \frac{\text{wt. of hydrogen in gms}}{\text{Mol. wt. of hydrogen}} = \frac{6}{2} = 3$$

$$R \text{ in litre-atm} = 0.082; T = (273 + 273) \text{ or } 546^\circ \text{A.}$$

$$\therefore 1.5 \times V = \frac{6}{2} \times 0.082 \times 546$$

$$\text{or } V = \frac{6 \times 0.082 \times 546}{2 \times 1.5} = 89.54 \text{ litres}$$

$$\therefore \text{vol. of hydrogen at the given conditions is } 89.54 \text{ litres}$$

(11) How many molecules are there in 10 litres of a gas at a pressure of 75 cm at 27°C?

Let V_1 be the volume of the gas at N. T. P. So, according to the relation $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$V_1 = \frac{P_2 V_2}{T_2} \times \frac{T_1}{P_1} = \frac{75 \times 10 \times 273}{(273 + 27) \times 76} = 8.98 \text{ litres}$$

Now, 22.4 litres at N. T. P. contain 6.023×10^{23} molecules

$$\therefore 8.98 \text{ " " " " " } \frac{6.023 \times 10^{23} \times 8.98}{22.4} \text{ molecules} \\ = 2.41 \times 10^{23} \text{ molecules}$$

Alternative method .

This result can also be arrived at from the relation $PV = nRT$.

If R is in litre-atm, P must be in atm and V in litres.

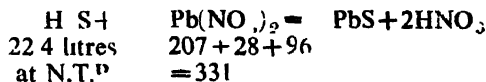
Now, $P = \frac{75}{76}$ atm ; $V = 10$ litres ; $T = 273 + 27 = 300$ A

$$R = 0.082 ; n = ?$$

$$\therefore \frac{75}{76} \times 10 = n \times 0.082 \times 300 \text{ or, } n = \frac{75 \times 10}{76 \times 0.082 \times 300} = 0.401 \text{ mole}$$

Now, number of molecules = number of moles \times Avogadro number
 $= 0.401 \times 6.023 \times 10^{23} = 2.41 \times 10^{23}$.

(12) Calculate the volume of hydrogen sulphide at 14°C and 760 mm pressure which will react with 10 gms of lead nitrate. (Pb = 207).



From the equation .

331 gms of lead nitrate react with 22.4 litres of hydrogen sulphide at N.T.P.

$$\therefore 10 \text{ " " " " " " } \frac{22.4 \times 10}{331} \text{ or } 0.677$$

litre of hydrogen sulphide at N.T.P.

Let V_2 be volume of H_2S at 14°C and 770 mm.

From the relation $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\frac{760}{273} \times 0.677 = \frac{770 \times V_2}{273 + 14} \text{ or } V_2 = \frac{760 \times 0.677 \times 287}{273 \times 770} = 0.703 \text{ litre.}$$

(13) Brass is an alloy of copper and zinc. A sample of brass weighing 5.793 gms. when treated with an excess of dilute sulphuric

acid gives 324 ml. of dry hydrogen at 20°C and 750 mm. pressure. What is the percentage by weight of copper in the alloy? (Zn 65.3)

Zinc dissolves in dilute sulphuric acid giving off hydrogen. Copper is unable to do so as it occupies a position below hydrogen in the electrochemical series.

Let V_1 be the volume of hydrogen at N. T. P.

∴ According to the relation $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$P_1 = 760 \text{ mm}$$

$$P_2 = 750$$

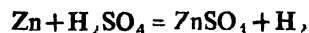
$$V_1 = ?$$

$$V_2 = 324 \text{ ml.}$$

$$T_1 = 273^\circ \text{A}$$

$$T_2 = (273 + 20)^\circ \text{A} = 293^\circ \text{A}$$

$$\therefore \frac{760 \times V_1}{273} = \frac{750 \times 324}{293} \quad \text{or, } V_1 = \frac{750 \times 324 \times 273}{293 \times 760} \text{ ml} = 298.0 \text{ ml}$$



$$65.3$$

$$22.4 \text{ litres at N.T.P.}$$

22400 ml of hydrogen are evolved by 65.3 gms. of zinc

$$\therefore \quad \begin{array}{ccccccc} 298 & \text{,,} & \text{,,} & \text{,,} & \text{,,} & \text{,,} & 65.3 \\ & & & & & & 22400 \end{array} \quad \frac{298}{22400} = 0.0133 \text{ gm.}$$

Weight of brass given = 5.793 gms

,, ,, zinc found = 0.8688 gm.

,, ,, copper = 4.9242 gms.

5.793 gms of brass contain 4.9242 gms of copper

$$\therefore \quad \begin{array}{ccccccc} 100 & \text{,,} & \text{,,} & \text{,,} & \text{,,} & & 4.9242 \times 100 \\ & & & & & & 5.793 \end{array}$$

or 85.002 gms of copper

∴ Weight of copper in the given alloy = 85.002%.

(14) A compound contains 37.8% of carbon 6.3% of hydrogen and 55.9% of chlorine. 0.638 gm of the compound when vapourised occupies a volume of 154 ml at 100°C and normal pressure. What is the molecular formula of the compound? What is its exact molecular weight? (Cl=35.5) [W. B. H S. 1979]

From the given data,

ratio of weights C : H : Cl = 37.8 : 6.3 : 55.9

$$\text{and } \text{,, } \text{,, } \text{atoms C : H : Cl} = \frac{37.8}{12} : \frac{6.3}{1} : \frac{55.9}{35.5}$$

$$= 3.15 : 6.3 : 1.575$$

$$= 2 : 4 : 1 \text{ (dividing each by the lowest number 1.575)}$$

∴ The empirical formula of the compound is $\text{C}_2\text{H}_4\text{Cl}$.

Now, from the relation $PV = nRT$,

$$1 \times 0.154 = \frac{0.638}{M} \times 0.082 \times 373 \quad (\text{where } M = \text{Mol. wt.})$$

$$\therefore M = \frac{0.638 \times 0.082 \times 373}{0.154} = 126.71$$

The molecular formula of the compound is $(C_2H_4Cl)_n$

(where n is a small whole number)

$$\therefore (C_2H_4Cl)_n = 126.71$$

$$\text{So, } n = \frac{\text{Mol wt}}{\text{Empirical formula wt}} = \frac{126.71}{24 + 4 + 35.5} = 2$$

(nearest whole number)

$$\therefore \text{Mol. formula of the compound} = C_4H_8Cl_2.$$

On Dalton's law of partial pressures :

(15) A gas mixture contains three volumes of oxygen and two volumes of chlorine at a pressure of 760 mm. Find the partial pressure of each of the gases.

Let p_{O_2} and p_{Cl_2} be the partial pressures of oxygen and chlorine respectively. Then, pressure of the gas mixture, $P = p_{O_2} + p_{Cl_2}$
 = 760 mm. Initial vol. of oxygen (V_0) = 3 and its changed vol (V) = 5
 ('.' Total vol. of the gas mixture = 3 + 2 = 5)

Now, according to Boyle's law,

$$p_{O_2} \times V = 760 \times V_0 \quad \text{or} \quad p_{O_2} = \frac{760 \times 3}{5} = 456 \text{ mm.}$$

Similarly, p_{Cl_2} is given by

$$p_{Cl_2} = \frac{760 \times 2}{5} = 304 \text{ mm}$$

(16) Calculate the partial pressures of oxygen and nitrogen present in air at N.T.P. Air contains 78% nitrogen and 21% oxygen by volumes

Let p_{O_2} and p_{N_2} be the partial pressures of oxygen and nitrogen respectively.

$$\therefore \text{Total pressure, } P \text{ of the gas mixture} = p_{O_2} + p_{N_2} = 760 \text{ mm.}$$

Here, initial vol. of oxygen = 21 and changed vol. oxygen in the mixture = 100.

Similarly, initial vol. of nitrogen = 78 and its volume in the mixture = 100.

$$\therefore \text{According to Boyle's law, } p_{O_2} = \frac{760 \times 21}{100} = 159.60 \text{ mm.}$$

$$\text{and } p_{N_2} = \frac{760 \times 78}{100} = 592.80 \text{ mm.}$$

(17) A glass cylinder of capacity 100 ml filled with oxygen under 160 mm is connected by a narrow tube and stop cock with another cylinder of capacity 400 ml filled with nitrogen under 200 mm. What will be the total pressure of the mixture at the same temperature?

Let p_{O_2} and p_{N_2} be the partial pressures of oxygen and nitrogen respectively.

Initial vol. of oxygen = vol. of the cylinder filled with oxygen = $V_1 = 100$ ml and Initial of nitrogen = vol. of the cylinder containing nitrogen = $V_2 = 400$ ml.

$$\therefore \text{Change in volumes of both gases} = V_1 + V_2 = (100 + 400) \text{ ml} = 500 \text{ ml}$$

\therefore According to Boyle's law,

$$p_{O_2} = \frac{160 \times 100}{500} = 32 \text{ mm and } p_{N_2} = \frac{200 \times 400}{500} = 160 \text{ mm.}$$

$$\therefore \text{Total pressure } P \text{ of the mixture} = p_{O_2} + p_{N_2} = (32 + 160) \text{ mm} = 192 \text{ mm}$$

(18) A sample of hydrogen collected over water in a gas-measuring tube has a volume of 40 ml. measured at 17°C temperature and 750 mm pressure. Calculate the volume of the dry gas at 0°C temp. and 760 mm. pressure. (Aqueous tension at 17°C is 14.4 mm).

Pressure of the dry gas = Atmospheric pressure — aqueous tension = $(750 - 14.4) \text{ mm} = 735.6 \text{ mm}$.

$$\begin{array}{ll} P_1 = \text{Initial pressure of dry hydrogen} = 735.6 \text{ mm} & P_2 = 760 \text{ mm} \\ V_1 = 40 \text{ ml} & V_2 = ? \\ T_1 = 273 + 17 = 290^\circ \text{ A} & T_2 = 273^\circ \text{ A} \end{array}$$

Substituting the values in the gas equation $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$, we have

$$\frac{735.6 \times 40}{290} = \frac{760 \times V_2}{273} \quad \text{or} \quad V_2 = \frac{735.6 \times 40 \times 273}{760 \times 290} = 36.45 \text{ ml.}$$

(19) A mixture of 20 gms of hydrogen and 80 gms of oxygen is kept in a vessel of 20 litre capacity at 27°C . What is the total pressure inside the vessel? (H = 1, O = 16) [W. B. H. S. 1982]

$$2 \text{ gms of hydrogen} = \frac{2}{2} = 1 \text{ mole of hydrogen}$$

$$8 \text{ gms of oxygen} = \frac{8}{32} = 0.25 \text{ mole of oxygen}$$

$$\text{Temperature } (T) = 273 + 27 = 300 \text{ A},$$

$$\text{Volume } (V) = 20 \text{ litres and } R = 0.082 \text{ litre/atm/deg/mole}$$

Let P_1 and P_2 be the partial pressures of hydrogen and oxygen respectively

Now applying the relation $PV = nRT$, we get

$$P_1 \times 20 = 1 \times 0.082 \times 300 = 1.23 \text{ atmospheres}$$

$$\text{and } P_2 \times 20 = 0.25 \times 0.082 \times 300 = 0.3075 \text{ atmospheres}$$

$$\therefore \text{Total pressure} = P_1 + P_2 = 1.23 + 0.3075 = 1.5375 \text{ atmospheres}$$

(20) A mixture consists of 0.7425 gram of a gas A of molecular weight 99.0, and 0.273 gram of a gas B of molecular weight 68.25, the total pressure is 76.2 cm of mercury. Calculate the partial pressures of A and B.

Let p_A and p_B be the partial pressures of the gases A and B respectively

$$\therefore 0.7425 \text{ gm of A} = \frac{0.7425}{99.0} = 0.0075 \text{ mole of A}$$

$$0.273 \text{ gm of B} = \frac{0.273}{68.25} = 0.0040 \text{ mole of B.}$$

Total number of moles = $0.0075 + 0.0040 = 0.0115$ The mole fractions of A and B are therefore

$$\frac{0.0075}{0.0115} \text{ and } \frac{0.0040}{0.0115} \text{ respectively}$$

$$\text{Partial pressure of A, } p_A = \frac{0.0075}{0.0115} \times 76.2 \text{ mm} = 497 \text{ mm.}$$

$$\therefore \text{Partial pressure of B, } p_B = 76.2 - 49.7 = 26.5 \text{ mm.}$$

(On the law of gaseous diffusion)

(21) Under the same conditions of temperature and pressure, 216 ml of a gas A escaped through a fine hole of a vessel in 18 minutes whereas 144 ml of another gas B (mol wt = 64) required 24 minutes to diffuse out of the same vessel. Find the molecular weight of A.

Let r_1, r_2 denote the rates of diffusion and M_1, M_2 the molecular weights of A and B respectively.

It is known that

$$\text{Rate of diffusion} = \frac{\text{Vol. of the gas (ml)}}{\text{Time (second)}}$$

$$\therefore r_1 = \frac{216}{18 \times 60} = 0.2 \text{ ml/second.}$$

$$\text{and } r_2 = \frac{144}{24 \times 60} = 0.1 \text{ ml/second}$$

According to Graham's law of diffusion,

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \quad \text{or,} \quad \frac{0.2}{0.1} = \frac{\sqrt{64}}{\sqrt{M_1}}$$

$$\text{or } \sqrt{M_1} = \frac{0.1}{0.2} \times \sqrt{64} = 4 \quad \text{or } M_1 = 16$$

(22) At standard conditions, 1 litre of hydrogen weighs 0.09 gm whereas 1 litre of oxygen weighs 1.44 gms (nearly). Which of the two gases diffuses faster? Calculate how much faster.

As per question, at STP, wt. of 1 litre of hydrogen = 0.09 gms or density of hydrogen = $d_H = 0.09/\text{litre}$; Similarly, the density of oxygen = $d_O = 1.44/\text{litre}$.

\therefore The lighter gas hydrogen (with low density) diffuses more quickly than oxygen which has greater density.

Let r_H and r_O be the rates of diffusion of hydrogen and oxygen respectively.

$$\therefore \text{According to the law of diffusion, } \frac{r_H}{r_O} = \sqrt{\frac{d_O}{d_H}}$$

$$\text{or } r_H = r_O \times \sqrt{\frac{d_O}{d_H}} \quad \text{or } r_H = r_O \sqrt{\frac{1.44}{0.09}} = r_O \times 4$$

\therefore The speed of diffusion of hydrogen is four times the speed of diffusion of oxygen.

(23) Equal volumes of hydrogen and oxygen take 24 and 96 seconds respectively to diffuse out of a porous wall. Calculate the molecular weight of oxygen.

Let V be the volume of hydrogen or oxygen.

$$\therefore \text{Rate of diffusion of hydrogen} = \frac{V}{24} = \frac{k}{\sqrt{d_H}} \quad (d_H = \text{density of hydrogen})$$

$$\text{and } \text{Rate of diffusion of oxygen} = \frac{V}{96} = \frac{k}{\sqrt{d_O}} \quad (d_O = \text{density of oxygen})$$

∴ According to the law of diffusion, $\frac{96}{24} = \frac{\sqrt{d_o}}{\sqrt{d_H}}$

$$\text{or, } \sqrt{d_o} = \frac{96}{24} \sqrt{d_H} = 4 \quad 1 = 4$$

∴ d_o = density of oxygen (relative) = $4^2 = 16$.

∴ Mol. wt. of oxygen = $2 \times 16 = 32$

Alternative method : We know

$$\frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}} \quad [t_1 \text{ and } t_2 \text{ denote the time of diffusion and } M_1 \text{ and } M_2 \text{ the molecular weights of hydrogen and oxygen respectively}]$$

$$\therefore \frac{96}{24} = \sqrt{\frac{M_2}{2}} \quad \therefore \sqrt{M_2} = 4 \sqrt{2}$$

$$\text{or, } M_2 = \text{Mol. wt. oxygen} = 16 \times 2 = 32.$$

(24) The rates of diffusion of two gases A and B are in the ratio of 0.29 : 0.271. The relative density of B is 25 ($H = 1$) ; what is the relative density of A ?

Let r_A, r_B denote the rates of diffusion and D_A, D_B the relative densities of A and B respectively.

$$\text{As per question, } \frac{r_A}{r_B} = \sqrt{\frac{D_B}{D_A}} \text{ or } r_A \times \sqrt{D_A} = r_B \times \sqrt{D_B}$$

$$\begin{aligned} \text{or, } 0.29 \times \sqrt{D_A} &= 0.271 \times \sqrt{25} \quad \text{or } \sqrt{D_A} = \frac{0.271 \times \sqrt{25}}{0.29} \\ &= \frac{0.271 \times 5}{0.29} \end{aligned}$$

$$\therefore D_A = 21.8.$$

(25) 16 c.c. of hydrogen are found to diffuse in 1 minute 40 seconds. What volume of sulphur dioxide will diffuse in the same time under the same conditions ? ($S = 32$)

Let r_1 and M_1 stand for the rate of diffusion and molecular weight respectively of hydrogen, and r_2 and M_2 for those of sulphur dioxide.

$$r_1 = \frac{16 \text{ c.c.}}{100 \text{ sec}} \text{ and } r_2 = \frac{V \text{ c.c.}}{100 \text{ sec}}$$

$$M_1 = 2 \text{ and } M_2 = 64.$$

$$\therefore \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \quad \text{or } \frac{16}{V} = \frac{\sqrt{64}}{\sqrt{2}} = \frac{8}{\sqrt{2}}$$

$$\therefore V = 2 \sqrt{2} = 2.83 \text{ c.c.}$$

(26) The rate of diffusion of hydrogen from a mixture of hydrogen and oxygen is 1 c.c./second. How long will 1 gm-molecule of oxygen take to diffuse? (Volume has been measured under standard conditions of temperature and pressure.)

Let r_H , r_O denote the rates of diffusion and M_1 , M_2 the molecular weights of hydrogen and oxygen respectively. Then according to the law of diffusion,

$$\frac{r_H}{r_O} = \sqrt{\frac{M_O}{M_H}}$$

$$\text{or, } r_O = r_H \sqrt{\frac{M_H}{M_O}} = 1 \sqrt{\frac{2}{32}} = \frac{1}{4} \quad \text{or } 0.25 \text{ c.c. /sec.}$$

At S. T. P., the vol. occupied by 1 gm-molecule of oxygen is 22.4 litres

Now, 0.25 c.c. diffuses in 1 sec

\therefore 22400 „, diffuse in $\frac{22400}{0.25 \times 60 \times 60}$ hrs.

or 24 hrs. 53 mins. 4 seconds

APPENDIX

Kinetic Theory of Gases

(Not included in W. B. H. S. Syllabus)

The common behaviour of the gases has so far been described in the light of the gas laws which are based on experiments quite independent of any theory of the nature of the gases. In order to establish a theoretical foundation for interpreting such behaviour of gases and to derive the gas laws mathematically, a simple theory known as the Kinetic theory of gases was put forward. This is extremely useful in physical chemistry and based on some fundamental assumptions, stated below.

Fundamental assumptions of the kinetic theory of gases : (1) A gas consists of a collection of a very large number of minute discrete particles called molecules. The molecules of a gas are further thought of as spherical, perfectly elastic particles. All the molecules of a gas are identical in mass, size and in all other respects but they differ from gas to gas.

(2) The molecules of gas within a container are believed to be in a state of ceaseless chaotic motion in all directions with high velocities continually colliding with each other and with the walls of the container. The molecules move in straight lines until on collision with another molecule or with the wall of the containing vessel the direction of motion is changed. Further, in spite of enormous number of collisions the molecular density in any volume remains undisturbed i.e. the molecules at one place is never found to collect in larger number than at another.

(3) The pressure which a gas exerts is due to the total effect of the continuous collisions of the moving molecules on the walls of the container. The average force per unit area which the molecules exert in their collisions with the walls per unit time is the pressure. The number of collision in unit time being very great, the pressure appears constant (at constant temperature). The gaseous diffusion also occurs as a result of the random motion of the molecules.

(4) The molecules are so minute particles that the total volume of the actual gaseous molecules may be considered negligible relative to the total volume of the gas.

(5) At relatively low pressures, the average distance between the molecules of gases are so large that the forces of attraction or repulsion between them may be neglected. The effect of gravity on the motion of the molecules is also negligible.

(6) The molecules behave as perfectly elastic bodies and there is no loss of kinetic energy (i.e. energy due to motion) for the gas as a whole resulting from the collisions of mutual frictions of the molecules.

(7) The average kinetic energy of the gas molecules in the system measures the temperature (absolute) of the gas. Hence, the absolute zero of temperature would be attained if all the molecules were reduced to a state of rest.

Explanation of the gas laws in the light of the kinetic theory
All the gas laws—Boyle's law, Charles' law, Avogadro's law, Dalton's law of partial pressures and the law of diffusion are in agreement with the kinetic theory of gases and can be explained with the help of this theory.

(A) **Boyle's law** According to the kinetic theory, gas pressure is exerted in the containing vessel as the result of the collisions between the gas molecules and the walls of the container. It follows, therefore, that the greater the number of molecules present in a given volume the greater will be the pressure. If the volume of a given quantity of gas is reduced at constant temperature, the average velocity of the gas molecules remain unaltered, so they collide more frequently with the walls of the smaller containing vessel. As a result

of more frequent collisions, the pressure is increased. Therefore, the diminution of volume of gas at constant temperature causes the pressure to increase proportionately. Thus, the volume of a given mass of a gas at constant temperature is inversely related to its pressure. This Boyle's law.

(B) **Charles' law**. The Charles' law is expressed in the form

$$\frac{v_1}{T_1} = \frac{v_2}{T_2} = \text{constant (at constant pressure)}$$

where v_1 and v_2 are the volumes of the gas at absolute temperatures T_1 and T_2 , respectively. This relationship can be accounted for in the light of kinetic theory. According to this theory, the temperature of the gas is proportional to the average kinetic energy of the gas molecules. Therefore, a fall of temperature represents a decrease in the average kinetic energy of the gas molecules that average molecular velocity decreases (mass remaining constant). If the pressure is kept constant, the decreased velocity causes the gas to occupy a smaller volume. This is to say that the volume of a given quantity of a gas at constant pressure directly varies as its temperature. This is Charles' law.

(C) **Dalton's law of partial pressures**. In terms of the kinetic theory, this law can be explained as follows.

In a non reactive mixture of two or more gases each gas exerts a separate pressure because of the collisions of its molecules with the walls of the container. This pressure, called the partial pressure, is obviously equal to the pressure caused by the collisions of the fixed number of molecules of the gas as if occupying the total volume of the container. Therefore the sum of all the collisions of the molecules of all the constituent gases gives rise to the total pressure of the gas mixture. This is Dalton's law of partial pressure.

(D) **Graham's law of diffusion**. The diffusive property of gases also depends on the fact that the gases consist of molecules in rapid motion in vacant space. Now the kinetic theory tells that the average kinetic energy (K.E.) of the molecules of any gas at a constant temperature is same. Thus, at constant temperature, for two gases A and B, average kinetic energy of the molecules of A = Average kinetic energy of the molecules of B.

Let m_1 and v_1 be the average mass and average velocity of the molecules of the gas A and m_2 and v_2 the average mass and velocity of the molecules of the gas B.

Then, the kinetic energy $= \frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2$ (when the temperature and pressure are constant).

$$\therefore m_1 v_1^2 = m_2 v_2^2 \text{ or } \frac{v_1^2}{v_2^2} = \frac{m_1}{m_2} \text{ or } \frac{v_1}{v_2} = \sqrt{\frac{m_1}{m_2}}$$

$$\frac{v_1}{v_2} = \sqrt{\frac{d_2}{d_1}} \quad [\because \text{mass is proportional to density (d)}]$$

This is a form of Graham's law of diffusion.

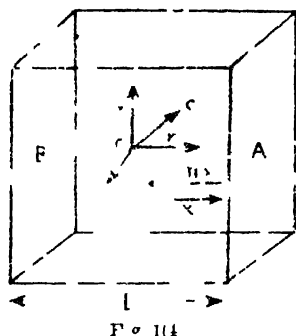
The equation for the pressure of a gas. The postulates of the kinetic theory enable us to calculate the pressure of a gas in terms of the number, mass and velocity of the molecules.

Let us consider n molecules of a gas, each of mass m are enclosed in a cubical vessel of l cm long [Fig 1(42)]. These molecules are moving constantly in all directions with different velocities striking the walls of the cube. Since it is difficult to ascertain the velocity of each molecule, let us assume them to have an average velocity represented by c .

Although the molecules are moving in every possible direction, their velocities at any moment can be resolved into three rectangular components x, y, z parallel to the three sides of the cubical container

$$\text{Then, } c^2 = x^2 + y^2 + z^2$$

Let us now study the case of a single molecule moving along x -axis between the two opposite sides A and B of the cube assuming the component of its velocity at right angle to that side is x . The collisions being perfectly elastic, the molecule after striking the side A with velocity x rebounds with exactly the same velocity x in opposite direction. So, the momentum of the molecule just when it strikes the side A mx and the momentum of the molecule after collision $-mx$.



Hence, the change of momentum due to each collision $mx - (-mx)$

$= 2mx$. Now l is the distance between the sides A and B. $\frac{l}{x}$ will be the time required for one collision and in unit time, the molecule will make $\frac{x}{l}$ collisions giving a change of momentum $2mx \times \frac{x}{l}$
 $= \frac{2mx^2}{l}$. Similarly, the change of momentum in unit time for the

other two components y and z in directions along y and z axes will be $\frac{2my^2}{l}$ and $\frac{2mz^2}{l}$ respectively

Hence, the change of momentum for one molecule in all directions in unit time is given by

$$\frac{2mx^2}{l} + \frac{2my^2}{l} + \frac{2mz^2}{l} = \frac{2m}{l} (x^2 + y^2 + z^2) = \frac{2mc^2}{l}$$

For n molecules in all directions, the total change of momentum will be $\frac{2mnc^2}{l}$. This represents the total pressure exerted by the gas on the six sides of the cube

Now the area of each side is l^2 cm and since there are six sides, the total area exposed to the gas pressure will be $6l^2$.

$$\text{So the pressure } P \text{ on unit area} = \frac{2mnc^2}{l} \div 6l^2 = \frac{2mnc^2}{6l^3}$$

But l^3 is the volume v of the cubical container

$$\text{Therefore, } P = \frac{mnc^2}{3v} \quad \text{or} \quad Pv = \frac{1}{3} mnc^2$$

This is known as the kinetic equation for gases

Although, this kinetic equation was derived on the assumption of a cubical vessel, it can be shown that the same result can be arrived at for a vessel, of any shape. The latter may be imagined to be partitioned in a large number of infinitesimal small cubes, the total volume of which gives the volume of the vessel of the particular shape

CHAPTER 9

CHEMICAL EQUILIBRIUM

✓ **Reversible Reactions :** It is a well-established fact that many reactions do not go to completion even if appropriate experimental conditions are maintained. They are found to proceed to a certain extent and then apparently stop leaving a small or considerable amount of the reactants unaffected.

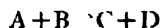
In many cases, it has also been proved that the products of a reaction themselves react forming the original reactants once more. Let us consider a general reaction of this type in which the reactants A and B form the products C and D at a given temperature.



Again, C and D react to regenerate A and B

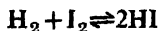


These two oppositely directed reactions are represented by a single equation as



Here, the sign of equality '=' has been replaced by the double oppositely directed arrows ' \rightleftharpoons ' called sign of reversibility. Such a reaction is called a reversible reaction. In fact, all chemical reactions are reversible in nature and can proceed in both directions. But in some cases the extent of the opposite reaction is so small as to be negligible and such reactions are said as proceeding to completion quite definitely in one direction. The reversibility of reactions can be detected when both the forward and the reverse reactions occur at noticeable extent. Generally, such reactions are described as reversible reactions. The most important criterion of a reaction of this type is that none of the reactants will get exhausted. When the reaction is allowed to take place in a closed system wherefrom none of the substances involved in the reaction can escape, we get a mixture of the reactants and the products in the reaction vessel. If hydrogen and iodine vapour are heated in a closed vessel at 450 C, they combine forming hydrogen iodide while hydrogen iodide itself decomposes at this temperature appreciably into its constituent elements hydrogen and iodine.

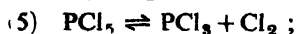
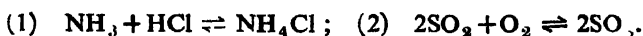
The reversible nature of the reaction is expressed by the equation



The reaction between acetic acid and ethyl alcohol leading to the formation of ethyl acetate and water is a well known reversible reaction in a liquid system.

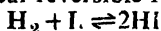


Some more familiar reversible reactions are stated below.



Every reversible reaction depending on its nature will after some time reach a stage when the reactants and the products coexist in a state of balance and their amounts will remain unaltered for unlimited time. Such a state of a chemical reaction is called *chemical equilibrium*. The point of such an equilibrium varies only with the temperature.

The attainment of equilibrium of the classical reversible reaction,



has been graphically shown in Fig. 1(13)

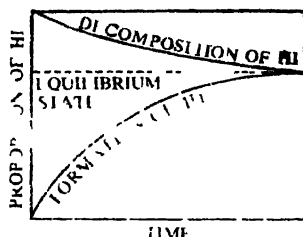


Fig 1(13)

✓ **Law of Mass Action.** It has been found that the rate of a chemical reaction depends definitely on the relative masses of the reacting substances. In general, the rate of a reaction indicates the quantity of the reactants transformed or the amounts of the products formed in unit time. The quantity of the reagents transformed is expressed in gm molecule and the unit of time is usually the second. Guldberg and Waage carried out a number of experiments showing the influence of the relative masses of the reacting substances on the reaction rates and expressed the experimentally observed facts in the form of a generalisation commonly known as *Law of Mass Action*. The law states :

The rate of a chemical change at any instant at a given temperature is directly proportional to the active mass of each of the interacting substances

If follows that the rate of the forward reaction will increase on increasing the active mass of any of the reactants, while the reverse reaction will go on with an enhanced rate if the active mass of any one of the products is increased.

The term *active mass* in a homogeneous system of gases or dilute solution refers to the molar concentration, that is, the number of gm-molecules of the substance in unit volume.

If a gms of a substance A of molecular weight M be present in V litres, then $\frac{a}{M}$ gm-moles of A are present in V litres.

∴ The active mass of $A = \frac{a}{M \times V}$

Therefore, the law of mass action may be stated alternatively as,

At constant temperature, the rate of a chemical reaction varies directly as the molar concentration of the reacting substances.

It is to be clearly understood that the rate of a chemical reaction is not proportional to the weights of the reacting substances present in the system but to the numbers of molecules of each kind present in a given volume. Now one gm-mole of any substance contains the same Avogadro Number of molecules (i.e. 6.023×10^{23}) and the concentration is therefore expressed as gm-molecules per litre.

Mathematical formulation of the Law of Mass Action : If A and B be the reacting substances and C and D the products of a simple reversible reaction, there are clearly two reactions in progress at the same time

(i) $A + B \rightarrow C + D$ (commonly known as forward reaction)

(ii) $C + D \rightarrow A + B$ (commonly called reverse reaction)

These two reactions are symbolised by the single equation



This equation expresses that A and B react to form C and D as products, which, on the other hand, interact to regenerate A and B.

According to the law of mass action, the rate of the forward reaction $r_{AB} \propto [A] [B]$

or, $r_{AB} = k_1 [A] [B]$ (where k_1 is the proportionality constant for forward reaction.)

And, the rate of the reverse reaction $r_{CD} \propto [C] \times [D]$

or, $r_{CD} = k_2 [C] [D]$ (k_2 is the proportionality constant of the reverse reaction)

[A], [B], and [D] stand for the molar concentrations of A, B, C and D respectively. The molar concentrations of substances taking part in the system may also be denoted by C_A , C_B , C_C and C_D

Now, at the beginning of the reaction between A and B, there will be no C or D. As soon as a little C and D are formed, the reverse reaction sets in. At first the forward reaction predominates but as C and D accumulate, the reverse reaction builds up. So in accordance with the law of mass action the rate of forward reaction gradually diminishes with time as the concentrations of A and B decrease owing to their conversion into C and D. As the reaction proceeds, more and more quantities of C and D will be present in the system and the speed of the reverse reaction gradually increases. A time will come when the speed of the forward reaction becomes equal to the speed of the reverse reaction ($r_{AB} = r_{CD}$). The system is then said to have attained a state of equilibrium and there

will be no further change in masses or the concentrations of the components of the system

The constancy of the composition of the mixture at equilibrium is not due to the fact that all chemical reactions have ceased entirely but is the net result of the balancing of two opposing reactions occurring at the same time with the same rate. This is why a chemical equilibrium is said to be a *dynamic equilibrium*. Evidently, such an equilibrium is dynamic in action but stationary in effect. A chemical equilibrium is dependent on the temperature

At equilibrium, $r_{AB} = r_{CD}$

$$\therefore k_1[A] \times [B] = k_2[C] \times [D]$$

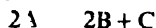
$$\text{or, } \frac{[C] \times [D]}{[A] \times [B]} = \frac{k_1}{k_2} = k \text{ (constant)}$$

The constant k is called the equilibrium constant or mass law constant which is the ratio of the product of concentrations of the reactants to the product of the concentrations of the substances produced. This may also be referred to as the ratio of the rates of the forward and reverse reactions. The value of constant depends on the temperature and the nature of the reaction. It has a fixed value for any specified reaction under a specified condition of temperature

NB (1) It is to be remembered that $[A]$ etc. indicate the unit concentrations. They are the molar concentrations (number of mol/litre) when the equilibrium is finally established

(2) We have seen in the above reaction the rate of the forward reaction $r_A = -\frac{1}{A} \frac{dA}{dt}$, if the molar concentrations of both A and B are unity then $r_{AB} = k_1$. Therefore, the rate of reaction is equal to the proportionality constant when all the reactants are of molar concentrations. This proportionality constant at this condition is said to be the specific reaction rate

So far, we have considered the process involving single molecule of each of the reactants and the products. If two or more molecules of the same substance take part they are to be regarded as separate molecular species and the value of the equilibrium constant may be determined accordingly. Thus the reaction



may be written as $A + A \rightleftharpoons B + B + C$

and so $r_A = k_1[A][A] = k[A]^2$

and $r_{BC} = k_2[B][B][C] = k_2[B]^2[C]$

At equilibrium, $\frac{[B]^2 \times [C]}{[A]^2} = \frac{k_1}{k_2} = k$ Equilibrium constant

For a general reaction represented by



the equilibrium constant

$$K = \frac{[G]^g \times [H]^h \times \dots}{[A]^a \times [B]^b \times \dots}$$

Here the coefficients in stoichiometric equation become the powers of the respective concentrations of the substances taking part in the reaction. This is the most generalised equation for the equilibrium constant and is also the most important form of the law of mass action. The equation states: the ratio of the product of the concentrations of the substances formed in a reversible reaction, each raised to the power of the number of its molecule involved in the reaction to the product of the concentrations of the reactants, each raised to the power equal to the number of its molecules taking part in the reaction is a constant at a fixed temperature.

Criteria of a chemical equilibrium :

(a) *Permanency* When at a given temperature a system attains the state of equilibrium, it does not change further with time i.e. the composition of the equilibrium mixture will remain unchanged for ever. Only a change of temperature can bring about a change in the equilibrium situation.

(b) *Approachability from both sides* The equilibrium condition of a reversible reaction is approached from either side of the reaction. At a fixed temperature, a given reversible reaction $A + B \rightleftharpoons C + D$ attains exactly the same state of equilibrium no matter whether we start with the reactants A and B or the products C and D.

(c) *The impertinence of the reaction* It is the chief criterion of the chemical equilibrium. A reversible reaction is never complete in any direction provided any of the products is not allowed to escape from the system. In other words, in equilibrium condition the reactants and the products are all present simultaneously in the reaction vessel.

Let us consider the reversible reaction $A + B \rightleftharpoons C + D$. Here A and B will react in the forward direction to produce C and D. As soon as a little C and D are formed the reverse reaction will start to generate A and B. Thus at equilibrium, all the four substances will remain. If one of the substances is taken to be vanished then its concentration automatically becomes zero and the value of the equilibrium constant k of the above reaction

$$k = \frac{[C] \times [D]}{[A] \times [B]}$$

will either be zero or infinity. Obviously,

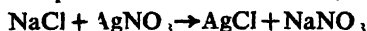
k in that case loses its significance.

Irreversible reactions Theoretically all chemical reactions are reversible. But there are many reactions in which the extent of the reverse reaction (i.e. combination of the products to produce the reactants) is so small as to be negligible. Such reactions which are ordinarily found to proceed to completion in one direction are said to be irreversible reactions e.g. decomposition of potassium chlorate.

$$2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$$

or, Decomposition of ammonium nitrate, $\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$

or, Precipitation of silver chloride,



In fact these and other similar reactions are also reversible in character and there is no existence of only irreversible reactions. It has been reasonably concluded that all so called irreversible reactions can be made to proceed in the reverse way if the right experimental conditions are set up. Let us consider a specific case when a mixture containing exactly two parts of hydrogen and one part of oxygen is exploded at ordinary temperature under the influence of electric spark, it is completely converted into water. There is no detectable residue of the reacting gases in the reaction vessel. But it has been found that at a temperature above 1500°C , water vapour is decomposed to an appreciable extent into hydrogen and oxygen. So the reverse reaction that occurs at high temperatures must take place even to a very small extent under ordinary conditions. So, the combination of hydrogen and oxygen to form water is regarded as an irreversible reaction under ordinary condition of temperature and pressure. But in fact it is also a reversible reaction.

Different forms of equilibrium constant— K_p and K_c . Generally, the equilibrium constant of a reversible reaction is represented by the symbol K . The equilibrium constant obtained by using molar concentration of each of the substances involved in the system is commonly denoted by K_c .

Thus, for a reaction $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$.

$$K = \frac{[\text{C}] \times [\text{D}]}{[\text{A}] \times [\text{B}]}$$

([A], [B], [C], [D] are the equilibrium concentrations of the reactants and the products)

In case of a gaseous reaction, the concentrations in the mass law equation may be substituted by the partial pressures of the components of the equilibrium mixture as the concentration of a gas is proportional to its partial pressure. The expression for the equilibrium constant in terms of partial pressures is symbolised by K_p . Therefore, if p_A, p_B, p_C, p_D be the partial pressures of A, B,

C and D respectively, then $K_p = \frac{p_C \times p_D}{p_A \times p_B}$

The relationship between K_p and K_c can easily be obtained as follows

From the relation $PV = nRT$ (discussed in chapter 8)

$$P = \frac{n}{V} RT = CRT \quad [C = \text{concentration}]$$

Accordingly, $p_A = [A] RT$, $p_B = [B] RT$ etc.

For a general reaction, $aA = bB + \dots + gG + hH + \dots$

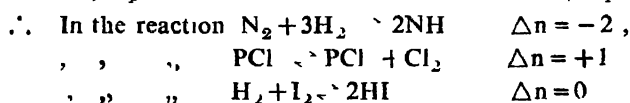
$$K_p = \frac{p_G^g \times p_H^h \times \dots}{p_A^a \times p_B^b \times \dots} = \frac{[G]^g \times [H]^h \times \dots}{[A]^a \times [B]^b \times \dots} (RT)^{(g+h+\dots) - (a+b+\dots)}$$

$$\therefore K_p = K_c (RT)^{\Delta n}$$

Where $\Delta n = (g + h + \dots) - (a + b + \dots)$ = change in the number of molecules (moles) during the reaction.

Number of molecules (moles) of the products—number of molecules (moles) of the reactants

For a reaction in which the number of molecules of the reactants is equal to the number of molecules of the products i.e. Δn is zero, K_p and K_c are identical. In other cases, $K_p \neq K_c$.



In a gaseous reaction, the components of the equilibrium mixture can also be stated in terms of mole fractions. We know that the partial pressure of a gas is equal to its mole fraction multiplied by the total pressure, i.e.

$p_A = x_A P$, $p_B = x_B P$ etc where x_A , x_B etc are the mole fractions of A and B respectively and the total pressure is P.

Le Chatelier's Principle: The state of a chemical equilibrium is dependent on certain conditions or factors such as temperature, pressure, concentrations of the reactants and products. How a system would behave if any of these conditions controlling the equilibrium be changed from its equilibrium value was first investigated by Le Chatelier. The valuable generalisation made by him is known as *Le Chatelier's principle*. The principle states:

"If a system is in equilibrium and one of the factors controlling the equilibrium is altered, the system will automatically tend to adjust itself in such a way so as to neutralise the effect of the change." In other words, if a change occurs in one of the conditions such as temperature, pressure, concentrations of the constituents under which a system is in equilibrium, the system will always react in such direction which will tend to counteract as far as possible the effect of that change. This rule is also called *Le Chatelier and Von Braun's principle*.

This principle qualitatively foretells the effect of variation of pressure, temperature or concentration on a system which is in

equilibrium or it summarises the idea that whenever the state of equilibrium of a system is affected by increase or decrease in one of its controlling factors then the other factors will change their values in order to restore the balance or position of equilibrium

✓ **The influence of pressure-change on the position of equilibrium of a gaseous reaction.** The influence of pressure-changes is much more noticeable in reactions taking place in gaseous state. When on a system at equilibrium pressure is increased, Le Chatelier principle demands that a change should take place in the system so that the additional pressure is relieved. This is only possible if the system tends to contract or brings about the reaction in the direction in which the volume of the system decreases. Consequently, increase of pressure favours a reaction in the direction in which it occurs with diminution in the number of molecules present at equilibrium. It is to be borne in mind that according to Avogadro's hypothesis the volume is directly proportional to the number of molecules.

The effect of the change in pressure on a reaction at equilibrium may be summarised as follows

Type of reaction	Effect of increase in pressure	Effect of decrease in pressure
(a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ Decrease in number of molecules left to right of 4 molecules of hydrogen and nitrogen yield 2 molecules of ammonia	Volume decrease. Increase of pressure favours the formation of more ammonia i.e. the equilibrium moves to the right	Volume increase. Decrease of pressure results in the breaking up of NH_3 into its elements i.e. position of equilibrium moves to the left
(b) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ Increase in number of molecules left to right	Increase of pressure decreases the dissociation	Decrease of pressure favours the dissociation
(c) $2O_3 \rightleftharpoons 3O_2$	I	I
(d) $N_2 + O_2 \rightleftharpoons 2NO$ No change in number of molecules	No change in volume. No effect of pressure on equilibrium position of equilibrium is maintained	No change in volume. Pressure has no effect on equilibrium position of equilibrium is maintained
(e) $H_2 + I_2 \rightleftharpoons 2HI$	Do	Do

✓ **The effect of temperature-change on the position of equilibrium**
If the temperature of a system at equilibrium is raised by supplying heat from outside, Le Chatelier's principle requires the equilibrium system to respond to oppose the temperature change i.e., the reaction will immediately proceed in a direction where heat will be absorbed. In short, an endothermic reaction should proceed to a greater extent by increase in temperature. Decrease of temperature, on the other hand, favours an exothermic reaction or a reaction which is accompanied with the evolution of heat will give better

yields of products at lower temperatures. It is to be remembered that for a reversible reaction if it is exothermic for a change in one direction, it is endothermic for its change to the opposite direction. The effect of temperature on a chemical equilibrium has been shown in the following table

Type of reaction	Increase of temp	Decrease of temp
Exothermic (left to right) (1) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ + 22 K Cal (2) $2SO_2 + O_2 \rightleftharpoons 2SO_3$ + 45.0 K. Cal	Increase of temperature decreases the formation of NH_3 or SO_3 and favours the decomposition of NH_3 or SO_3 , i.e. new equilibrium has more of reactants	Favours the increased formation of NH_3 or SO_3 , i.e. new equilibrium in either of the cases has more products in the forward reaction
Endothermic (left to right) (1) $N_2 + O_2 \rightleftharpoons 2NO$ - 44.0 K. Cal $N_2O_4 \rightleftharpoons 2NO_2$ - 12.26 K. Cal	Favours formation of NO Favours dissociation of N_2O_4 i.e. new equilibrium in either of the cases has more of products in the forward reaction	Tends to reverse the reaction Do i.e. new equilibrium in either of the two cases has more of reactants in the forward reaction.

The effect of concentration-change or of addition of a component

If any one of the substances present in an equilibrium reaction is added from outside without change in any of the other conditions, then according to Le Chatelier's Principle the position of equilibrium will move to decrease the concentration of the added substance. To do so, the reaction will go in the direction in which the added substance is used up. For example



If some chlorine is added from outside, its partial pressure will evidently be increased. With the increase of the numerator, denominator should also increase in order to maintain the value of K_p constant i.e. the equilibrium is displaced towards the left (with formation of some PCl_5). Similarly in the reaction,



contained in a vessel at a given temperature if extra nitrogen is pumped into the same vessel, the position of equilibrium will shift from left to right i.e. there will be a greater proportion of nitric oxide in the new equilibrium mixture. Here, the partial pressure of nitrogen is increased and to keep the value of K_p constant, more nitric oxide will have to be formed

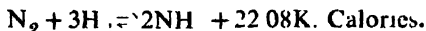
In a similar manner, if any of the substances taking part in a chemical equilibrium is removed, then, in accordance with Le Chatelier's Principle, the position of equilibrium changes to produce more of that substance.

✓ **The effect of an inert gas on equilibrium :** If a non-reacting gas be added into a system, the point of equilibrium may remain unaffected or may be displaced according to the conditions of addition. Addition, at constant volume, increases the total pressure but will not change the partial pressures of the reactants and the products. So, in this case, the introduction of an inert gas i.e. a gas which does not directly participate in the reaction makes no effect on the equilibrium point

The situation will be otherwise if the addition is made into the system at constant pressure. For a given total pressure the presence of an inert gas decreases the partial pressures of the substances involved in the reaction. The net result will be the same as if the gases at equilibrium were subjected to a lower pressure. In other words, it increases the volume to decrease the concentrations of the reactants and the products. Thus, in accordance with Le Chatelier's principle the presence of an inert gas will favour the reaction that takes place with an increase in volume (or the number of molecules).

✓ **Some industrial applications of Le Chatelier's Principle :**

(1) **Manufacture of ammonia by Haber's Process :** The large scale preparation of ammonia by Haber's synthetic process uses the reaction



It is a reversible, exothermic reaction. It is evident from Le Chatelier's principle that *low temperature favours the production of ammonia*. Increase of temperature will cause ammonia to dissociate into N_2 and H_2 with absorption of heat supplied. But lowering of temperature increases the yield but reduces the rate of the reaction. Consequently, the reaction requires a longer period of time to attain equilibrium. So, it becomes necessary to select a high temperature at which the reaction proceeds at a workable speed giving an appreciable yield of ammonia. The temperature thus chosen is known as *optimum temperature*. We know that a catalyst can influence the speed of a chemical reaction to a great extent. It is also known that the catalyst does not affect the position of equilibrium as it has equal effects on the forward and the reverse reactions in a reversible process. The optimum temperature for synthesis of ammonia from its elements has been found to be 550°C if reduced iron mixed with some powdered molybdenum (promoter) is used as a catalyst.

It appears from the equation that the reaction is accompanied by a diminution in volume (hence the number of molecules). So, according to Le Chatelier's Principle, *high pressure will favour the production of ammonia*.

In practice, a total pressure of 200 atmospheres is applied in Haber's process. That the yield of ammonia is increased with higher pressure can be shown mathematically.



Let us start with 1 gm-mole of nitrogen and 3 gm-moles of hydrogen and at equilibrium let α be the fraction (in terms of moles) of nitrogen that has reacted to produce ammonia. Then, 2α moles of ammonia will remain in the equilibrium mixture.

\therefore The final system will contain $(1-\alpha)$ mole of nitrogen, $(3-3\alpha)$ moles of hydrogen and 2α moles of ammonia and total moles in the system will be $4-2\alpha$. Now, if P be the total pressure and p_{N_2} , p_{H_2} , p_{NH_3} be the partial pressures of nitrogen, hydrogen and ammonia respectively, then,

$$p_{\text{N}_2} = \frac{1-\alpha}{4-2\alpha} P; \quad p_{\text{H}_2} = \frac{3-3\alpha}{4-2\alpha} P \quad \text{and} \quad p_{\text{NH}_3} = \frac{2\alpha}{4-2\alpha} P.$$

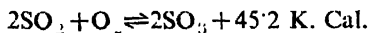
$$\therefore K_p = \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} \times p_{\text{H}_2}^3} = \frac{\left[\frac{2\alpha}{4-2\alpha} P \right]^2}{\left[\frac{1-\alpha}{4-2\alpha} P \right] \left[\frac{3-3\alpha}{4-2\alpha} P \right]^3} = \frac{4\alpha^2(4-2\alpha)^2}{27(1-\alpha)^4 P^2}$$

It follows from the above equation that if pressure be raised, the production of ammonia will increase in order to maintain the equilibrium.

It is to be kept in mind that if NH_3 formed at the high pressure and temperature is removed immediately from the reaction vessel, the equilibrium position will change to produce more of NH_3 .

(2) Large scale preparation of sulphur trioxide :

Sulphur trioxide is prepared by oxidising sulphur dioxide with oxygen. This is the first and the most important step in the manufacture of sulphuric acid by contact process. The reaction is :



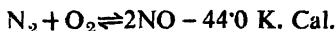
It is a reversible, exothermic reaction. So, Le Chatelier's principle demands that the yield of sulphur trioxide is greater when the temperature is lower. But lowering of temperature reduces the reaction rate and so increases the time required for the production of sulphur trioxide. Thus the above conversion, at low temperature is not advantageous in an industrial operation. In contact process, the reaction is conducted at 450°C (optimum temperature) in presence of finely divided platinum used as a catalyst. If the product (SO_3) is removed from the sphere of action as soon as it is formed more and more reactants will combine to form SO_3 .

It appears from the above equation that the reaction is accompanied by a decrease in volume or number of molecules. Therefore, use of high pressure will improve the yield. It can be proved by considering K from the relation,

$$K_P = \frac{p_{\text{SO}_3}^2}{p_{\text{SO}_2}^2 \times p_{\text{O}_2}}$$

But if the conversion is made at the above working conditions the increase of pressure makes no appreciable improvement of the yield. Hence in industry, the process is worked at ordinary pressure.

(3) **Synthesis of nitric oxide** Nitric oxide is prepared by the combination of atmospheric nitrogen and oxygen. It is the main step in the manufacture of nitric acid by Birkeland and Ede process.



It is a reversible, endothermic reaction. It is clear that numbers, of molecules are equal on both sides of the equation and hence the yield will remain unaffected by a change of pressure.

Moreover, according to Le Chatelier's principle, high temperature favours the production of nitric oxide. Actually, nitrogen and oxygen are made to combine at a temperature of 3000°C produced with the help of an electric arc.

Further, if the equilibrium mixture is cooled very quickly to temperatures lower than 1500°C , the formation of nitric oxide is greatly enhanced as its decomposition at these temperatures becomes too small. Some reversible reactions are discussed in detail here.

Reactions without change in the number of molecules :

(a) **Formation of hydrogen iodide from its elements** It is a familiar reversible reaction in which the number of molecules of the reactants (hydrogen and gaseous iodine) is the same as the number of molecules of the product (HI)



Suppose, initially we start with a moles of hydrogen and b moles of iodine. If x gm-moles out of a moles of hydrogen react to form hydrogen iodide at equilibrium then the equilibrium mixture will contain $2x$ gm-moles of hydrogen iodide and the relative amounts of hydrogen, iodine and hydrogen iodide will be $(a-x)$, $(b-x)$ and $2x$ gm-moles respectively.

$$\therefore \text{Total gm-moles present in the system} = a - x + b - x + 2x = a + b$$

If p stands for total pressure and v for the volume of the reaction vessel, then at equilibrium, the molar concentrations and the partial

pressures of the substances taking part in the reaction will be given by

Substance	Molar concentration	Partial pressure
H_2	$\frac{a-x}{v}$	$\frac{a-x}{a+b}P = p_{H_2}$
I_2	$\frac{b-x}{v}$	$\frac{b-x}{a+b}P = p_{I_2}$
HI	$\frac{2x}{v}$	$\frac{2x}{a+b}P = p_{HI}$

Now, the values of K_C and K_P are :

$$K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)} = \frac{4x^2}{(a-x)(b-x)} \quad \text{and}$$

$$K_P = \frac{p_{HI}^2}{p_{H_2} \times p_{I_2}} = \frac{\left(\frac{2x}{a+b}P\right)^2}{\left(\frac{a-x}{a+b}P\right)\left(\frac{b-x}{a+b}P\right)} = \frac{4x^2}{(a-x)(b-x)}$$

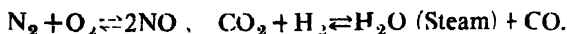
The equilibrium constants K_C and K_P are the same.

It is to be noted that the volume v or the pressure p has disappeared from the final result : the equilibrium constant is independent of the volume or pressure at a given temperature. Now, starting with equal number (a) of moles of reactants we have :

$$K_P = K_C = \frac{4x^2}{(a-x)(a-x)} = \frac{4x^2}{a^2 - x^2}$$

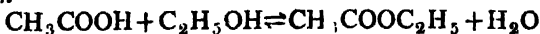
The reaction is an endothermic one and the formation of hydrogen iodide will increase by an increase in temperature.

Similarly, it may be shown that the equilibrium constants of the following reactions are not influenced by a change of pressure or volume.



(b) Formation of ester from acetic acid :

The reaction between acetic acid and ethyl alcohol to form ethyl acetate (ester) is a familiar example of homogeneous equilibrium in liquid system.



Initial moles a b 0 0

At eqm moles $a-x$ $b-x$ x x

Suppose, a gm-moles of acetic acid and b gm-moles of alcohol are initially mixed. If x be the gm-moles of ester formed and v the volume

of the system at equilibrium, then, the molar concentrations, of the different components will be given by

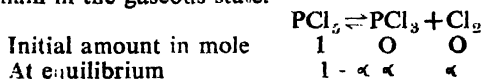
$$\begin{aligned} [\text{CH}_3\text{COOH}] &\rightarrow \frac{a-x}{v}; [\text{C}_2\text{H}_5\text{OH}] \rightarrow \frac{b-x}{v} \\ [\text{CH}_3\text{COOC}_2\text{H}_5] &\rightarrow \frac{x}{v}; [\text{H}_2\text{O}] \rightarrow \frac{x}{v} \\ \therefore K_C &= \frac{[\text{CH}_3\text{COOC}_2\text{H}_5] \times [\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}] \times [\text{C}_2\text{H}_5\text{OH}]} = \frac{\frac{x}{v} \times \frac{x}{v}}{\frac{a-x}{v} \times \frac{b-x}{v}} = \frac{x^2}{(a-x)(b-x)} \end{aligned}$$

Here, the volume is eliminated from the equation for the equilibrium constant. So, the position of equilibrium is independent of the total volume of the system.

Reactions that occur with change in the number of molecules :

(c) **Dissociation of phosphorus pentachloride :**

Phosphorus pentachloride on being dissociated gives phosphorus trichloride and chlorine. All the substances involved in the reaction remain in the gaseous state.



Let us start with 1 gm-mole of PCl_5 . Let α be the fraction of PCl_5 dissociated at equilibrium, then the equilibrium mixture will contain $(1 - \alpha)$ gm-mole of PCl_5 , α gm-mole of PCl_3 and α gm-mole of Cl_2 .

The total gm-moles in the system = $1 - \alpha + \alpha + \alpha = 1 + \alpha$

If P and v represent the total pressure and volume of the system respectively, then the molar concentrations and partial pressures of the substances participating in the reaction are given below.

Substance	Molar concentration	Partial pressure
PCl_5	$\frac{1-\alpha}{v}$	$\frac{1-\alpha}{1+\alpha}P = p_{\text{PCl}_5}$
PCl_3	$\frac{\alpha}{v}$	$\frac{\alpha}{1+\alpha}P = p_{\text{PCl}_3}$
Cl_2	$\frac{\alpha}{v}$	$\frac{\alpha}{1+\alpha}P = p_{\text{Cl}_2}$

$$\therefore K_C = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{\frac{\alpha}{v} \times \frac{\alpha}{v}}{\frac{1-\alpha}{v}} = \frac{\alpha^2}{(1-\alpha)v}$$

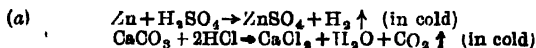
$$\text{and } K_p = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{\left(\frac{\alpha}{1+\alpha}P\right) \times \left(\frac{\alpha}{1+\alpha}P\right)}{\frac{1-\alpha}{1+\alpha}P} = \frac{\alpha^2}{1-\alpha^2}P$$

Here, $K_p \neq K_c$. Since K_p is constant at a given temperature, it follows from the equation of the equilibrium constant that α or the fraction of dissociation decreases when the pressure (P) is increased. So the point of equilibrium is dependent on the pressure. It is thus possible to calculate α provided the value of K_p is known.

This reaction is an endothermic one and the extent of dissociation is increased when the temperature is raised.

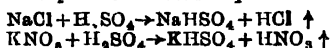
N.B. Almost all chemical reactions are reversible in nature. But under certain conditions, many of the reactions are found to go up to completion.

We know that a chemical equilibrium can exist only in a closed system where all the reacting substances and the products remain present. When one of the products is allowed to escape from the sphere of action as soon as it is formed, the reverse reaction cannot occur and the reaction proceeds to completion in forward direction only. Such a reaction is then regarded as a one-sided or irreversible one. A few of the reactions which are almost irreversible in nature will be considered here briefly.



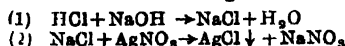
In the first double decomposition process stated above, metallic zinc reacts with dilute sulphuric acid producing gaseous hydrogen as one of the products. In the second case, carbon dioxide gas is formed as a result of reaction between calcium carbonate and HCl. When these reactions are conducted in open vessels, both hydrogen and carbon dioxide gas is formed as a result of reaction between calcium carbonate and HCl. When these reactions are conducted in open vessels, both hydrogen and carbon dioxide escape into the atmosphere as soon as they are formed. Consequently, the partial pressure of hydrogen or carbon dioxide may be taken as almost 0 (zero), and the reactions will proceed continually from left to right in order to maintain fixed values of the equilibrium constants.

Sometimes, an important product of a double decomposition reaction is found to be more volatile than the other compounds concerned and is driven off by heating either as gas or as the vapour of a volatile liquid. For example,



When the mixture of solid sodium chloride and conc. sulphuric acid is heated, hydrogen chloride is removed from the sphere of action and the reaction goes to completion in the forward direction. The reaction between the solid potassium nitrate and conc. sulphuric acid is an irreversible process due to escape of nitric acid as its vapour.

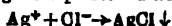
(b) Many reactions especially those occurring in solution, go to virtual completion. Such reactions are regarded as taking place between the compounds which are fully ionised. Let us consider the following cases :



The reaction (1) between hydrochloric acid and caustic soda is a simple case of neutralisation of a strong acid by a strong base or *vice-versa*. In aqueous solution this reaction remains completely a one-sided one. Here, the reactants hydrochloric acid remains completely as H^+ and Cl^- ions and sodium hydroxide as Na^+ and OH^- ions. We have already discussed that the process of neutralisation is essentially a reaction between H^+ and OH^- ions produced from an acid and an alkali respectively forming undissociated molecules of water.

Due to the formation of almost undissociated molecules of water, H^+ and OH^- are constantly removed from the sphere of action. The ionic concentrations of ions produced from the dissociation of water are so small as to be negligible. So, the combination of H^+ and OH^- ions is regarded as proceeding in one direction.

In the reaction (2), both the salts are present completely as ions in aqueous solution. NaCl produces Na^+ and Cl^- ions and AgNO_3 is dissociated as Ag^+ and NO_3^- ions. When a solution containing silver nitrate (Ag^+ and NO_3^-) is added to one containing sodium chloride (Na^+ and Cl^-) silver chloride precipitates out. The essential change is represented as



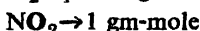
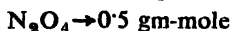
Ions Na^+ and NO_3^- remain in solution.

The very low solubility of silver chloride suppresses any possible reverse with the dissolved ions and the reaction becomes virtually irreversible.

Numerical examples

(1) The equilibrium constant for the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ at 497°C is 636. At what pressure, will N_2O_4 be 50% dissociated?

If we start with 1 gm-molecule of N_2O_4 , then at equilibrium



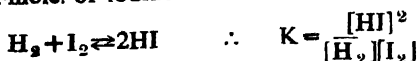
\therefore Total moles, = 1.5

\therefore Partial pressure of $\text{N}_2\text{O}_4 = p_{\text{N}_2\text{O}_4} = \frac{0.5}{1.5}P$ and $p_{\text{NO}_2} = \frac{1}{1.5}P$

(P = total pressure)

$$\therefore K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}} = \frac{\left(\frac{1}{1.5}P\right)^2}{\frac{0.5}{1.5}P} \quad \therefore 636 = \frac{P}{0.75} \quad \text{or, } P = 477 \text{ mm}$$

(2) If the value of the equilibrium constant (K) for the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ be 55.5 at 460°C , how much HI would be present at the equilibrium. We start with 1 gm-mole of hydrogen and 0.75 gm-mole of iodine.



Let x mol of each of hydrogen and iodine has disappeared at equilibrium producing $2x$ mols. of hydrogen iodide, then molar concentration of HI , $[\text{HI}] = 2x$, $[\text{H}_2] = 1 - x$ and $[\text{I}_2] = 0.75 - x$

$$\therefore K = 55.5 = \frac{4x^2}{(1-x)(0.75-x)} = \frac{4x^2}{0.75 - 1.75x + x^2}$$

$$\text{or, } 41.625 - 97.126x + 55.5x^2 = 4x^2$$

$$\text{or, } 51.5x^2 - 97.126x + 41.625 = 0$$

$$\text{or, } x^2 - 1.88x + 0.808 = 0$$

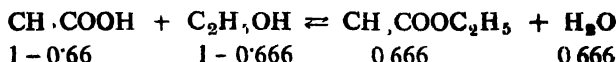
$$\therefore x = 0.72 \text{ mole.} \quad \text{Therefore } 2x = 1.44 = \text{Amount of HI}$$

[From algebra, we know that $ax^2 + bx + c = 0$.

$$\text{or, } x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}. \quad \text{On Solving the equation, two values}$$

of x are obtained. The other value found in this case is inadmissible as it exceeds the amount of reactants taken.]

(3) When 1 gm-mole of acetic acid and 1 gm-mole of ethyl alcohol are mixed together, 0.666 gm-mole of the acid is converted into the ester at the equilibrium condition. Calculate how much ester will be formed if one mole of acetic acid is treated with 0.5 mole of alcohol.



$$\begin{aligned} \therefore K &= \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} \\ &= \frac{(0.666/V) \times (0.666/V)}{(0.333/V) \times (0.333/V)} = 4 \text{ (nearly)} \end{aligned}$$

If x gm-moles of the ester be formed, then according to the question,

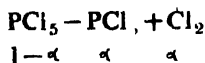
$$K = \frac{x^2}{(1-x)(0.5-x)} = 4 \quad \therefore 4 = \frac{x^2}{(1-x)(0.5-x)}$$

This is a quadratic equation which on solution gives two values of x , one is 0.423 and the other 1.57. The value 1.57 is inadmissible as 0.5 gm-mole of alcohol can never yield 1.57 moles of the ester.

\therefore number of moles of ester formed is 0.423

(4) At a temperature of 180°C and a total pressure of 1 atm. phosphorus pentachloride is dissociated to the extent of 41.7%. Calculate K_p of the reaction

When 1 gm mole of PCl_5 is taken and the extent of dissociation is α , then $(1-\alpha)$ gm-mole of PCl_5 , α -moles of PCl and α moles of Cl_2 will remain in the system at equilibrium



\therefore Total number of moles present $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$ and the partial pressures of PCl_5 , PCl , and Cl_2 are

$$p_{\text{PCl}_5} = \frac{1-\alpha}{1+\alpha}P, p_{\text{PCl}} = \frac{\alpha}{1+\alpha}P, p_{\text{Cl}_2} = \frac{\alpha}{1+\alpha}P \quad [P = \text{total pressure}]$$

$$\therefore K_p = \frac{p_{\text{PCl}} \cdot p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{\left(\frac{\alpha}{1+\alpha}P\right) \cdot \left(\frac{\alpha}{1+\alpha}P\right)}{\left(\frac{1-\alpha}{1+\alpha}P\right)} = \frac{\alpha^2 P}{1-\alpha^2} = \frac{(0.417)^2}{1 - (0.417)^2} \times 1 = 0.21$$

(5) 2 gm-moles of PCl_5 were heated in a closed flask of 2 litre-capacity. At equilibrium, PCl_5 is dissociated to the extent of 40%. Find the value of the equilibrium constant

$$40\% \text{ of } 2 \text{ gm-moles} = \frac{40 \times 2}{100} = 0.8 \text{ gm-mole}$$

∴ At equilibrium the reaction, $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$

the molar concentration of $\text{PCl}_5 = \left[\text{PCl}_5 \right] = \frac{2 - 0.8}{2} = 0.6 \text{ gm-mole}$

“ “ “ “ $\text{PCl}_3 = \left[\text{PCl}_3 \right] = \frac{0.8}{2} = 0.4 \text{ gm-mole}$

and “ “ “ “ $\text{Cl}_2 = \left[\text{Cl}_2 \right] = \frac{0.8}{2} = 0.4 \text{ gm-mole}$

$$K = \frac{0.4 \times 0.4}{0.6} = 0.267$$

GROUP B
INORGANIC CHEMISTRY
(NON-METALS AND THEIR COMPOUNDS)

CHAPTER 1

OXYGEN AND HYDROGEN

OXYGEN

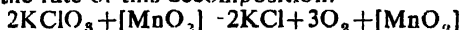
Symbol O Molecular formula O ₂ Position in the periodic table VIB,	Atomic weight 16.00 Atomic number 8 Electronic configuration 1s ² 2s ² 2p ⁴
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Scheele discovered oxygen in 1774 and called it 'vital air'. In the same year, Priestley discovered it independently by heating red oxide of mercury and called it dephlogisticated air. But its chemical nature, particularly its importance in combustion and respiration was first recognised by Lavoisier who named it oxygen, meaning acid producer. He proved that the products obtained by heating many non-metals like sulphur, carbon, phosphorus in oxygen reacted with water to produce acids.

In the free or uncombined state, oxygen exists to the extent of 21% by volume or 23% by weight in the air. It is the most essential element to the life of plants and animals.

Preparation of oxygen : Some compounds rich in oxygen, water and air are used as the sources for preparation of oxygen.

✓ **(A) Laboratory method of preparation :** In the laboratory, oxygen is prepared by heating an intimate mixture of powdered potassium chlorate and manganese dioxide. Potassium chlorate undergoes thermal decomposition producing oxygen and potassium chloride. Manganese dioxide simply acts as a positive catalyst* and increases the rate of this decomposition.



A mixture of 4 parts by weight of potassium chloride and 1 part by weight of manganese dioxide is taken in a hard glass test tube fitted with a cork through which passes a fairly wide, bent delivery tube. The tube is then clamped to a stand in a horizontal but slightly inclined to downwards position. A passage is left over the mixture along the length of the tube for free escape of oxygen.

The other end of the delivery tube is dipped under water in a pneumatic trough. The test tube is then carefully and uniformly heated (the end near the cork is heated first) when potassium chlorate decomposes to produce oxygen. Oxygen thus liberated passes through the delivery tube and begins to evolve through the water in the form of bubbles. The gas is allowed to escape for sometime till the air inside the test tube and the delivery tube has been driven out. Now a gas-jar completely filled with water is inverted over the bee-hive shelf of the trough so that the end of the delivery tube reaches the mouth of the jar through an opening. The

* Definition and explanation of catalysts have been given in page 12.

evolved oxygen collects inside the jar by downward displacement of water. Several jars of oxygen may be collected by applying the same procedure.

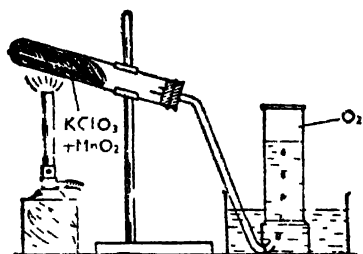


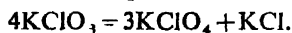
Fig. 2 (1) Preparation of oxygen in the laboratory

Oxygen prepared in this way may contain in slight amounts chlorine, carbon dioxide, water vapour as impurities. To purify the gas, it is first passed through a concentrated solution of caustic potash when chlorine and carbon dioxide are absorbed and then through conc sulphuric acid or phosphorus pentoxide to free it from water vapour. Pure and dry

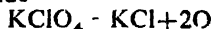
oxygen is finally collected by the displacement of mercury. ✓

Precaution : (i) Comparatively pure manganese dioxide freed from carbon particles and antimony sulphide must be used. Manganese dioxide contaminated with powdered carbon may cause serious explosion when heated with potassium chlorate, (ii) The half of the test tube used in the preparation should be kept vacant for easy escape of oxygen. (iii) The mouth of the test tube must be kept slightly inclined to downwards position so that the water from the trough may not enter the heated tube easily and crack the same. (iv) Heating must be done uniformly. (v) The end of the delivery tube is to be kept over water after the collection of the gas to prevent the entry of water in the hot tube from the trough.

✓ **Role of manganese dioxide in the preparation of oxygen from potassium chlorate :** When heated alone, potassium chlorate decomposes to give off oxygen. But this decomposition occurs at a fairly high temperature and in two stages. At first, at about 360°C, it liberates a small amount of oxygen and is rapidly converted into potassium perchlorate and potassium chloride.



With the rise of temperature (near about 610°C), the mass becomes pasty and at 630°C decomposes producing oxygen and potassium chloride



But in presence of manganese dioxide, the thermal decomposition of potassium chlorate takes place at a much lower temperature (200–240°C) and the oxygen is evolved much more steadily.

Manganese dioxide acting as a positive catalyst accelerates the decomposition of potassium chlorate but does not suffer any change in mass, chemical properties and composition. ✓

The catalytic effect of manganese dioxide on the decomposition of potassium chlorate can be proved by the following experiment.

A weighed quantity of a mixture of potassium chlorate and manganese dioxide (in the ratio of 4 : 1) is taken in a hard glass test tube. Into each of two other tubes, an approximately equal bulk of potassium chlorate and manganese dioxide alone are taken separately. Three tubes are then surrounded with sand on a sand-tray so that they are close together and vertical. Now the sand-tray is heated slowly.

It is found that at a considerably lower temperature, the gaseous oxygen is freely evolved from the tube that contains the mixture when there is no sign of any gas from either of the other tubes. A glowing chip of wood is immediately rekindled when it is brought near the mouth of the tube from which oxygen comes out. This proves that the evolved gas is oxygen. The tube is then allowed to cool and the residue is treated with water. Potassium chloride goes completely into the solution while manganese dioxide is left undissolved. The undissolved manganese dioxide is recovered by filtration, washed several times with water and finally dried in an air-oven. It is then weighed. The weight of manganese dioxide thus obtained is found to be equal to the weight of manganese dioxide originally taken. This MnO_2 can again be used for decomposing fresh quantities of KClO_3 . Further, on heating with conc. hydrochloric acid, this manganese dioxide gives the greenish yellow gas chlorine. Thus, it is proved that manganese dioxide plays the role of a catalyst and chemically remains unchanged after the reaction.

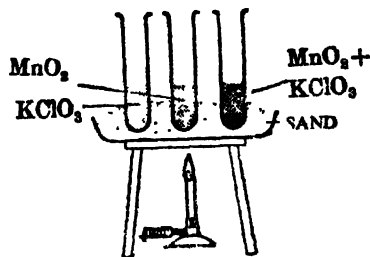
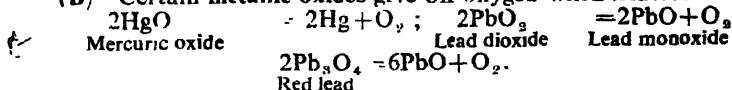


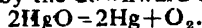
Fig. 2(1A) Role of manganese dioxide in the decomposition of potassium chlorate

Besides manganese dioxide, some other metallic oxides such as cupric oxide, ferric oxide etc. also act as catalysts in the decomposition of potassium chlorate. However, manganese dioxide is the most effective and widely used catalyst in this decomposition. It may be stated here that although manganese dioxide remains chemically unchanged it undergoes slight physical changes. It is more finely divided and brown when the reaction is over. From these physical changes, some chemists suggest that the catalyst enters into reaction by taking up oxygen from the chlorate to form an unstable intermediate higher oxide which then decomposes into oxygen and the original manganese dioxide.

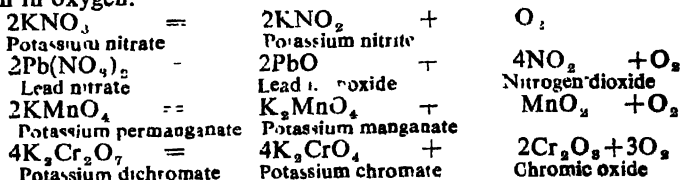
(B) Certain metallic oxides give off oxygen when heated.



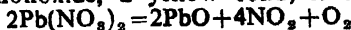
Oxygen from mercuric oxide : Red mercuric oxide is taken and heated in a hard glass test tube fitted with a bent delivery tube. Mercuric oxide thermally decomposes producing mercury and oxygen. The gaseous oxygen passes through the delivery tube and is collected as usual by the downward displacement of water.



(C) Oxygen may be obtained by strongly heating many salts rich in oxygen.



Oxygen from lead nitrate : The white crystals of lead nitrate decomposes to give off gaseous oxygen and nitrogen dioxide when heated. Lead monoxide, a yellow solid, is also formed at the same time.



Dry lead nitrate is taken in a hard glass test tube fitted with a delivery tube. The delivery tube is then connected with one limb of a U tube kept immersed in a freezing mixture (a mixture of ice and common salt). Another delivery tube is attached to the other limb of the U tube and its free end is kept under water. The test tube is then gradually heated when oxygen

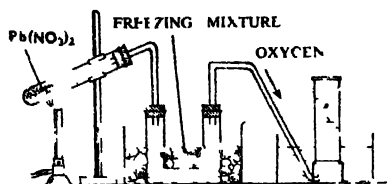


FIG. 2(2) Preparation of oxygen from lead nitrate

along with brown nitrogen dioxide gas passes through the U-tube. Nitrogen dioxide condenses to a brown liquid and remains in the U-tube while oxygen comes out of the other delivery tube and is collected by the downward displacement of water.

(D) Oxygen can be obtained by heating certain oxy-acids such as concentrated nitric acid and concentrated sulphuric acid.

Oxygen from concentrated nitric acid When concentrated nitric acid is allowed to fall drop by drop on red hot pumice stone it decomposes into oxygen, brown nitrogen dioxide gas and steam.



A distilling flask, half filled with pumice stone is fitted with a dropping funnel. The side tube (delivery tube) of the flask is connected to one limb of a U-tube kept immersed in a freezing mixture. The other limb of the U-tube is attached to a bent delivery tube, the end of which is placed under water. The flask is then strongly heated and concentrated nitric acid is poured from the dropping funnel by drops on the red hot pumice stone. The acid is thermally decomposed to produce a mixture of oxygen, nitrogen dioxide and steam, the mixture is allowed to come out of the delivery tube and is passed through the U-tube in which nitrogen dioxide and steam condense and remain in the tube in the liquid form. Oxygen passes on and is collected as usual by the displacement of water.

Similarly, oxygen can be obtained from concentrated sulphuric acid by allowing it to drop on the red hot pumice stone. The decomposition of conc. H_2SO_4 at the high temp. is expressed by the following equation

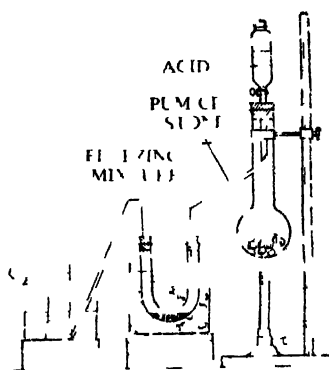
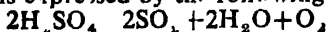
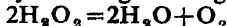


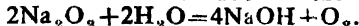
FIG. 2(3) Oxygen from oxy-acid

In this case, a mixture of sulphur dioxide, oxygen and steam comes out of the delivery tube and enters into the cooled U-tube where sulphur dioxide and steam condense to liquid. Oxygen passes out and is collected over water.

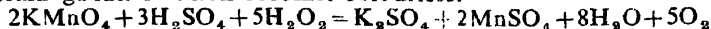
(E) Oxygen may be obtained easily from hydrogen peroxide or a metallic peroxide. Hydrogen peroxide decomposes spontaneously into water and oxygen even at the ordinary temperature. The rate of this decomposition is increased by application of heat or in presence of a catalyst like ground glass, manganese dioxide or platinum etc.



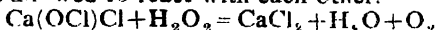
When sodium peroxide reacts with water, oxygen is readily evolved. The solution reacts alkaline due to the formation of sodium hydroxide.



Dropwise addition of hydrogen peroxide solution into a solution of acidified potassium permanganate liberates oxygen in the pure form. The other products formed in this reaction are potassium sulphate, manganous sulphate and water. The pink potassium permanganate solution becomes colourless.



The oxygen is set free when bleaching powder and hydrogen peroxide are allowed to react with each other.



(1) **Preparation of oxygen at ordinary temperature :** Oxygen may be prepared at the ordinary temperature by dropping (1) water on sodium peroxide or (2) hydrogen peroxide solution into a solution of potassium permanganate acidified with dilute sulphuric acid.

Sodium peroxide is taken in a conical flask fitted with a delivery tube and a dropping funnel containing water. Water is added to sodium peroxide drop by drop when oxygen comes out rapidly through the delivery tube and is collected by the displacement of water.

An alternative preparation in the same apparatus is the drop by drop addition of hydrogen peroxide solution from the dropping funnel to a solution of potassium permanganate in dilute sulphuric acid taken in the conical flask. A rapid evolution of oxygen occurs. Oxygen thus liberated is collected by the displacement of water.

(2) **Preparation of oxygen**

from water : (a) Electrolysis of water (being made slightly alkaline) with iron or nickel electrodes liberates oxygen at the anode. (b) Steam, on being treated with gaseous chlorine, gives off oxygen together with hydrogen chloride.

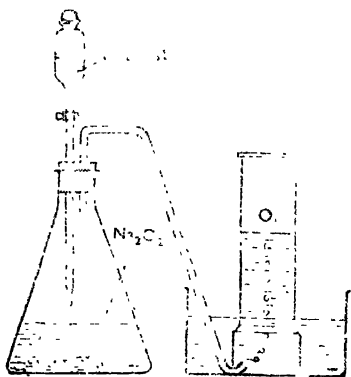
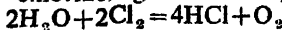


Fig. 2 (4) Preparation of oxygen at the ordinary temperature

(3) **Preparation of oxygen from air** : Air is a mechanical mixture containing mainly nitrogen and oxygen ($\frac{4}{5}$ part by volume of nitrogen and $\frac{1}{5}$ part by volume of oxygen). The main constituents of the mixture (e.g. oxygen and nitrogen) can be separated by fractional distillation of liquid air. Hence, air can be used as a source in the large scale preparation of oxygen.

This process of preparation involves the following steps :

- (1) Removal of carbon dioxide and moisture from the air ;
- (2) Liquefaction of air at low temperature and high pressure ;
- (3) Separation of oxygen and nitrogen by fractional distillation of liquid air.

Air is first freed from carbon dioxide and moisture by passing it through solid caustic potash and concentrated sulphuric acid in succession. Dry air is then brought under very high pressure by means of a compressing pump and is cooled by running water. Joule and Thomson showed that if a gas under high pressure is forced to come out through a small hole and is allowed to expand suddenly to a lower pressure, the issuing gas suffers a fall in temperature. This phenomenon is known as Joule-Thomson effect. This effect (i.e. sudden expansion and consequent cooling) is utilised in the liquefaction of air. The compressed air is pumped down a jacketted copper spiral tube under high pressure from which it is allowed to escape through a nozzle controlled by a valve and expand to almost atmospheric pressure. The air, cooled due to the Joule-Thomson effect circulates through the jacket round the spiral tube and cools further the incoming compressed gas. On repeating the cycle of compression and expansion several times, the temperature of the expanding air finally falls below -190°C and the air is condensed to a liquid. It is mainly a mixture of liquid nitrogen and liquid oxygen. Liquid nitrogen boils at -195°C and liquid oxygen at -183°C .

Now, on fractional distillation of the liquid air in a specially designed apparatus, more volatile nitrogen comes out first and finally almost pure oxygen remains in the distilling vessel. The liquid oxygen is evaporated, compressed and stored in steel cylinders.

Properties of oxygen—Physical : (1) Oxygen is a colourless, odourless, tasteless, neutral gas which can be liquefied to a pale blue liquid (b.p -183°C) at the low temperature by compression. On further cooling, it can be converted to a blue solid (m.p -281.4°C). (2) It is a little heavier than air. (3) It is only slightly soluble in water which dissolves 4% by volume of oxygen at 0°C . Hence, fish and other aquatic animals can live in water containing this dissolved oxygen.

Chemical : Oxygen is an exceptionally active element.

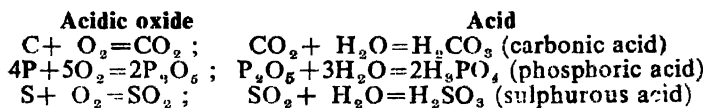
(1) *It shows allotropy*. The allotropic modification of oxygen is ozone.

* Definition and explanation of allotropy have been given in page 14 of this chapter.

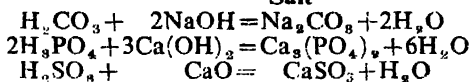
(2) *Oxygen is not combustible but is a supporter of combustion** of other substances. During combustion, a substance is oxidised by oxygen. Wood, wax, kerosene etc. continue to burn in the gas when ignited. Metals like sodium, potassium burn in moist air spontaneously.

(3) Many non-metals and metals combine directly with oxygen to form oxides either at the ordinary temperature or when heated with the evolution of heat and light. In the formation of the oxides, oxygen acts as an oxidising agent.

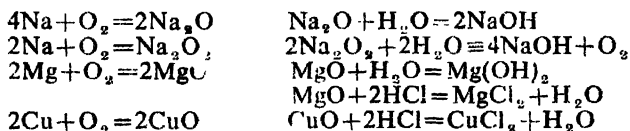
The non-metals like carbon, phosphorus, sulphur etc. burn in oxygen with bright flames and form acidic oxides. The oxides when dissolved in water produce acids, react with bases to form salts and turn blue litmus solution red.



Salt



Heated sodium burns in oxygen with a bright yellow flame and forms basic oxides. (i.e. sodium oxide and sodium peroxide). Burning magnesium continues to burn in oxygen with a dazzling flame and produces an oxide which is feebly basic in nature. Strongly heated copper combines with oxygen, giving the black, basic cupric oxide. The metallic oxides react with acids to give salts and water and the aqueous solutions of soluble metallic oxides react alkaline and turn red litmus blue.



A jet of hydrogen burns in oxygen with a blue flame, producing water. $2H_2 + O_2 = 2H_2O$.

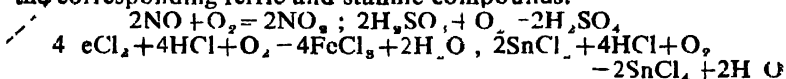
Non-metals like chlorine, bromine, iodine and metals like gold, platinum etc. do not combine with oxygen directly.

It is to be noted here that oxygen means acid producer. The oxides formed by burning carbon, sulphur, phosphorus etc. in oxygen are acidic in nature and react with water to form acids. Because of these, the gas was named oxygen by Lavoisier. But the use of the name is not appropriate in the following cases.

* The term combustion is applied to any chemical combination accompanied by evolution of heat and often light in which one or more of the reactants are gaseous. Combustions in oxygen or in air are so familiar that combination of a substance with oxygen evolving heat and light is commonly known as combustion. In the phenomenon of combustion, the substance which burns is referred to as 'combustible' and the atmosphere surrounding the burning substance is known as a supporter of combustion. The two terms are relative. The combustible material is oxidised by the supporter of combustion during combustion.

Metals like sodium, potassium, magnesium when burnt in oxygen give oxides which react with water producing alkaline solutions. Again, hydrogen burns in oxygen forming water which is neutral in character.

(4) Oxygen does the function of an oxidising agent either by uniting directly with a substance or by increasing the proportion of electronegative element of a compound. Colourless nitric oxide gas combines directly with oxygen forming brown fumes of nitrogen dioxide. Sulphurous acid is oxidised by oxygen to sulphuric acid. Oxygen oxidises acidified solutions of ferrous and stannous salts to the corresponding ferric and stannic compounds.



In many reactions, the oxidising power of oxygen is enhanced considerably in presence of catalysts. Thus, sulphur dioxide and ammonia can be oxidised by oxygen to sulphur trioxide and nitric oxide respectively in presence of platinum catalyst.



(5) The alkaline solution of potassium pyrogallate absorbs oxygen and the colour of the solution becomes brown. Due to absorption of oxygen, ammoniacal solution of cuprous chloride turns blue on exposure to air.

Experiments to prove the important properties of oxygen

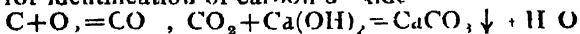
(1) *Oxygen is not combustible but is a supporter of combustion of other substances.* A glowing chip of wood is introduced into a jar of oxygen. The chip is immediately rekindled i.e., it bursts into flame but the gas does not burn.

(2) *Some non-metals burn in oxygen to produce acidic oxides.*

(a) A piece of charcoal taken on a deflagrating spoon is heated in a Bunsen flame till it glows. This piece of glowing charcoal is then introduced into a jar of oxygen, charcoal burns brightly combining vigorously with oxygen to give carbon dioxide. The spoon is taken out and the contents of the jar are shaken with water. The solution thus produced turns blue litmus slightly red and turns clear lime water milky. This shows that carbon burns in oxygen to produce carbon dioxide which dissolves in water giving an acidic solution. Carbon dioxide or its aqueous solution turns lime water milky due to the formation of white insoluble calcium carbonate. This serves as a test for identification of carbon dioxide.



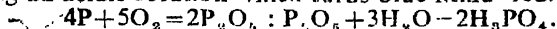
Fig 2(5)
Deflagrating
spoon



(b) In a similar manner, a piece of feebly burning sulphur is inserted into a gas-jar of oxygen. Sulphur burns more brightly with its characteristic bluish white flame and fumes of sulphur dioxide having a peculiar suffocating odour are

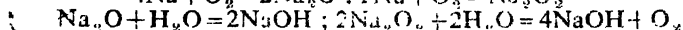
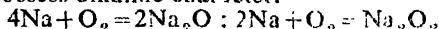
given off. A little water is added in the jar and shaken. A portion of the aqueous solution is treated with a few drops of blue litmus solution, the colour of the indicator turns red. A piece of paper soaked in acidified solution of potassium dichromate when added to this solution is turned green. Sulphur dioxide is detected by these tests.

(c) When a piece of burning yellow phosphorus taken on a deflagrating spoon is introduced in a jar of oxygen, phosphorus burns with a dazzling flame, emitting dense white cloud of phosphorus pentoxide. When shaken with water, the oxide dissolves giving an acidic solution which turns blue litmus red.

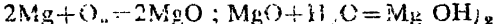


(3) *Some metals burn in oxygen to form metallic oxides most of which are basic in character*

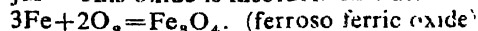
(a) A small piece of sodium taken on a deflagrating spoon is heated until it begins to burn. The burning sodium is then introduced into a jar of oxygen. The metal continues to burn more brilliantly with a golden yellow flame. The residue left after the reaction is dissolved in water. This aqueous solution turns red litmus blue. This proves that the oxides formed by burning sodium in oxygen possess alkaline character.



(b) A piece of burning magnesium ribbon is inserted into a jar of oxygen by means of tongs. The metal burns with a more dazzling flame and leaves a white ash of magnesium oxide which possesses slightly alkaline character. The solution obtained by boiling this ash with water turns colourless phenolphthalein solution red.



(c) The bottom of a gas-jar full of oxygen is covered with a layer of sand. A piece of iron wire tipped with a little sulphur (or carbon) is heated in a Bunsen flame until the sulphur begins to burn and is plunged quickly in the gas-jar of oxygen. The iron wire burns, giving off a shower of sparks and finally brown ferrous ferric oxide is deposited at the bottom of the jar. This oxide is insoluble in water.



(4) *Alkaline potassium pyrogallate solution absorbs oxygen.* A test tube filled with oxygen is inverted in alkaline potassium pyrogallate solution. The solution enters the tube slowly and fills it up completely. The colour of the solution becomes brown. This proves that oxygen is absorbed by alkaline pyrogallate solution which rises up the tube to fill up the vacuum caused due to absorption.

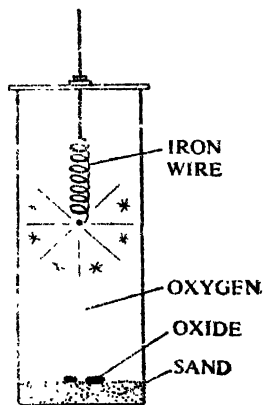


Fig. 2(6) Burning of iron in oxygen

✓ **Uses of oxygen.** (1) Oxygen is largely used in producing oxy-hydrogen and oxy-acetylene flames, for generating lime light. A mixture of hydrogen and oxygen when lighted at the mouth of a narrow tube produces an intensely hot flame (temperature about 2000°C) known as oxy-hydrogen flame. It is used in the production of lime light. Oxygen and acetylene on being burnt together gives

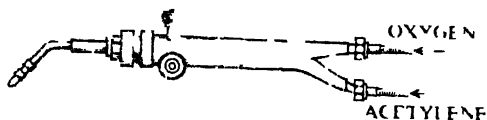
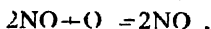


Fig. (7) Oxy acetylene torch

oxy-acetylene flame (temp. reaches about 3200°C) which is used for welding and cutting even very thick steel plates. (2) It is used in the industrial methods of preparation of sulphuric acid and nitric acid. (3) Oxygen is used in the artificial respiration of patients suffering from breathing troubles, or when anaesthetics are administered to patients. It is also used as an aid to breathing where natural supply of oxygen is insufficient, for example, in high-altitude flying or climbing in submarine etc. Generally liquid oxygen is used in these cases. (4) Liquid oxygen soaked in finely powdered charcoal is used as a blasting explosive in mines. (5) Oxygen is also used in the preparation of vanishes and for making steel in the new L-D process.

Test for oxygen (1) It rekindles a glowing chip of wood. This test generally distinguishes it from all other gases except nitrous oxide (N_2O).

(2) It forms brown fumes of nitrogen dioxide when it reacts with the colourless nitric oxide (NO).



Nitrous oxide has no effect on nitric oxide.

(3) Alkaline potassium pyrogallite solution turns brown on absorbing oxygen.

Catalyst –Catalysis

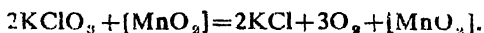
It is sometimes observed that the velocity of many chemical reactions is altered (either accelerated or decelerated) by the presence of a foreign substance (other than the reactants) which remains chemically unchanged at the conclusion of the reaction. Substances possessing the ability of affecting the rate of reactions are termed catalysts or catalytic agents.

✓ A catalyst is, therefore, defined to be a substance which by its mere presence, even in small quantity, influences the speed of a chemical reaction, itself remaining unchanged in mass and chemical composition.

at the end of the reaction and the process in which the rate of a chemical reaction is increased or decreased considerably by introducing a small quantity of a foreign substance which takes no part directly in the reaction is designated as catalysis.

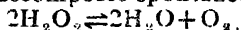
The catalyst which enhances the speed of a reaction is called a *positive catalyst* while the catalyst retarding the reaction rate is known as a *negative catalyst*. The negative catalysts are also referred to as inhibitors.

In the laboratory, oxygen is prepared by heating a mixture of potassium chlorate and manganese dioxide. Here, manganese dioxide acts as a positive catalyst. It causes the decomposition of KClO_3 to occur rapidly at a lower temperature but itself remains unchanged in amount and chemical nature.



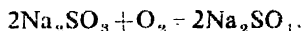
Finely divided platinum is used as a positive catalyst in the combination of sulphur dioxide and oxygen to yield sulphur trioxide. $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$. Powdered iron acts as a positive catalyst in the industrial preparation of ammonia from hydrogen and nitrogen.

Hydrogen peroxide decomposes spontaneously into oxygen and water.



The rate of this decomposition is slowed down if a minute quantity of sulphuric acid is added to it. Here, sulphuric acid acts as a negative catalyst.

Sodium sulphite is readily oxidised to sodium sulphate by oxygen.



But this oxidation can be retarded by introducing a minute amount of glycerine which acts as an inhibitor.

Characteristic features of catalysis : (1) The function of a catalyst is to accelerate or retard the speed of a chemical reaction but the catalyst itself suffers no change in mass and chemical composition. It may change its physical nature during a reaction, e.g. coarsely powdered manganese dioxide used in the preparation of oxygen may become fine powder at the end of the reaction.

(2) The presence of a very small amount of a catalyst can influence appreciably the speed of the reaction. A minute quantity of reduced iron (powder) can bring about the combination of large quantities of nitrogen and hydrogen to produce ammonia.

(3) The catalyst can never start a reaction which does not take place at all. It only accelerates or retards the speed of the reaction which occurs either extremely slowly or rapidly.

(4) In a reversible reaction, a given catalyst influences both the forward and the backward reactions equally without affecting the final state of equilibrium.

(5) One of the outstanding features of catalysts is their

specificity. Generally, a substance which acts as catalyst for a particular reaction fails to catalyse another. It is true that some substances are found to catalyse more than one reaction but it is not the case that catalysts can be interchanged between reactions at will.

Sometimes, it so happens that the activity of a catalyst is appreciably enhanced by the addition of a small quantity of another substance which itself is not a catalyst. Such a substance is known as a promoter. Thus, the promoter is a non-catalytic substance which is able to increase the activity of a catalyst to which it is added in relatively small amount. In the manufacture of ammonia, the catalyst used is powdered iron promoted by potassium and aluminium oxides or molybdenum powder.

Again, the catalytic activity of a given catalyst is sometimes reduced to a marked extent or lost completely by the traces of foreign substances. Such substances having the power of inhibiting or even completely destroying the efficiency of the catalysts are referred to as **catalytic-poisons** and the phenomenon is known as poisoning of catalysts. In the manufacture of sulphur trioxide from sulphur dioxide and oxygen, finely divided platinum is a suitable catalyst. But dust or arsenious oxide is a poison and it completely destroys the activity of the platinum catalyst.

Auto catalysis : So far, the catalysts have been regarded as foreign substances added to the reacting system. However, it is sometimes observed that one of the products formed during the reaction acts as a catalyst for that reaction. This phenomenon is called auto catalysis.

The reaction between potassium permanganate and hot oxalic acid solution in presence of dilute sulphuric acid is very slow at the start but it proceeds very rapidly as soon as a little manganous sulphate is formed as a result of interaction of the reactants. Here, Mn^{++} ions catalyse the reaction.

Allotropy

It is a well known fact that under suitable conditions, some elementary substances may exist in more than one form having distinct differences in their properties (mainly physical).

Ordinary gaseous oxygen as present in air or prepared by chemical methods is diatomic i.e. a molecule of oxygen consists of two atoms of the element. Now, chemical union of three atoms of oxygen gives rise to the molecule of another gaseous substance known as ozone. So the formulae of oxygen and ozone are O_2 and O_3 respectively. In fact, both oxygen and ozone are two different forms of the same element. But the two forms differ in many of their characteristic properties.

The property by virtue of which an element can exist in two or more forms in the same physical state differing mostly in physical

properties and in some chemical ones is called allotropy. The different forms of the element are known as allotropic modifications or allotropes

Usually the less familiar form is marked as the allotropic modification of the element. Thus, ozone is an allotrope of oxygen. Besides oxygen, the allotropic forms of carbon, sulphur and phosphorus are well known.

Allotropy arises either (i) due to the difference in the number of atoms in the molecule or (ii) due to the difference in the mode of arrangement of atoms in the molecule. The first case is illustrated by O_2 and O_3 . In the second case, the different allotropes will contain the same number of atoms in the molecule as observed in carbon and sulphur. The difference in the amount of available energy is sometimes regarded as one of the causes of allotropy.

Allotropic modifications of carbon, phosphorus and sulphur will be discussed in detail later.

HYDROGEN

Symbol H ,	At. wt. 1.008
Molecular formula H_2 ,	Atomic number 1
Position in the periodic table 1A or VII B (disputed)	Electronic configuration $1s^1$

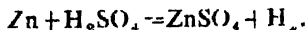
Sir Henry Cavendish (1776) was the first to establish that hydrogen was a distinct substance. He called it inflammable air. Lavoisier (1783) proved its elementary nature and named it hydrogen (meaning water producer) as it produced water on burning in air.

In the free state, it does not occur in nature in any appreciable extent. In the uncombined state it exists in traces only in many volcanic and other natural gases and in the atmosphere of the sun. But the element occurs in vast quantities in the combined state in such compounds as water, acids, alkalis and most organic substances.

Preparation of hydrogen: Hydrogen is prepared from acids, alkalis and water.

(1) From acids:

(A) Laboratory method of preparation: Hydrogen is most commonly prepared in the laboratory by the action of granulated zinc on dilute sulphuric acid. Zinc replaces the hydrogen of the acid and produces zinc sulphate.



Some pieces of granulated zinc (commercial) are taken in a two-necked Woulfe's bottle fitted with gas-tight corks. Through one of them passes a thistle funnel reaching almost to the bottom of the bottle and through the other a bent delivery tube is introduced. Water is poured down the thistle funnel so that the end of the funnel and whole of zinc dip under the water. The lower part of the delivery tube must be kept well above the surface of water.

As hydrogen forms an explosive mixture with oxygen of the air, the apparatus must perfectly be made air-tight first. Having done

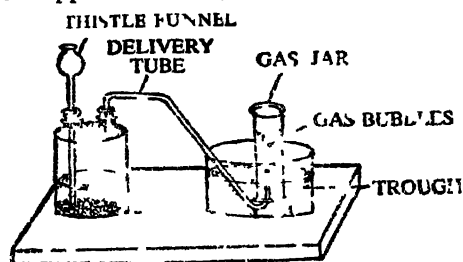


Fig. 7(8) Preparation of hydrogen in the laboratory. Hydrogen gas evolves at the ordinary temperature and begins to come out through the delivery tube. The gas is allowed to escape as effervescence for some time to ensure complete removal of air from inside the Woulfe's bottle and the delivery tube. When the air is completely driven out, a gas-jar completely filled with water is inverted over the end of the delivery tube dipped under water. The gas jar must not contain any air inside. Hydrogen collect in the jar by the downward displacement of water. A gas jar of hydrogen may similarly be collected.

Precautions. During the preparation and collection of hydrogen by this process some precautions are to be taken.

(i) The end of the thistle funnel and granulated zinc must remain under the surface of the liquid in the Woulfe's bottle. (ii) Gas tightness must be used. The apparatus must be completely air tight. (iii) Test for it, air is blown from the mouth through the free end of the delivery tube when water rises up the stem of the thistle funnel. The end of the delivery tube is then closed by the finger. If the apparatus is fully air-tight the surface of water in the funnel will remain stationary and will show no tendency to descend gradually. (iv) Before collecting hydrogen, the gas must be allowed to escape for some time so that whole air inside the apparatus is driven out. To ensure this a test tube is filled up with hydrogen by the displacement of water. Closing the tube with the thumb it is brought near a Bunsen flame. If it burns with a sound, the gas is free from air indicating that air has been completely removed from the apparatus. (v) The gas jar, used in collecting the gas must not contain any air bubble. (vi) A flame should be kept nearby as hydrogen explodes violently with air if a flame catches the mixture.

In connection with the preparation of hydrogen, the following points are also to be kept in mind.

(i) Perfectly pure metals do not react with sulphuric acid or reacts to produce hydrogen very slowly at ordinary temperature. The reaction is extremely slow for many factors relative to the electrolytic nature of the metallic zinc. So granulated zinc (cold anode) is preferably used. If it is copper sulphate solution is added to the zinc, zinc is covered with a thin layer of copper. The resulting zinc-copper couple reacts readily with dilute acid and evolve hydrogen. (2) During the reaction between zinc and dilute sulphuric acid a part of the acid gets reduced to sulphur dioxide. Therefore, cold and dilute sulphuric acid is used. (3) In place of dilute sulphuric acid, dilute hydrochloric acid can also be used. Hydrogen liberated by the action of metals on concentrated hydrochloric acid is impure and will invariably contain fumes of volatile hydrogen chloride. Thus conc. hydrochloric acid is unsuitable for liberation of hydrogen.

Purification of hydrogen. Hydrogen prepared by the action of commercial zinc on dil sulphuric acid is not pure. It contains impurities like hydrogen sulphide (H_2S), phosphine (PH_3), arsine (AsH_3), sulphur dioxide (SO_2), carbon dioxide (CO_2), oxides of nitrogen, moisture in small quantities. It also contains traces of nitrogen. This impure hydrogen gas may be purified by passing it in succession through a series of U-tubes containing the following reagents -

- (a) Lead nitrate solution to absorb H_2S
- (b) Silver sulphate solution to absorb PH_3 and AsH_3
- (c) Solid caustic potash to absorb CO_2 , SO_2 and oxides of nitrogen
- (d) Conc sulphuric acid or phosphorus pentoxide to arrest moisture

However hydrogen is not so easily freed from nitrogen.

To remove nitrogen, the gas is passed in an evacuated glass bulb containing palladium filings which absorb hydrogen and not nitrogen. Nitrogen is then pumped out of the bulb. On heating the bulb to dull redness pure hydrogen comes out. Hydrogen thus purified is collected by the downward displacement of mercury.

Preparation of very pure hydrogen On electrolysis a dilute, warm solution of barium hydroxide in a U-tube made of glass fitted with nickel electrodes, hydrogen is liberated at the cathode. Actually, water undergoes electrolysis producing hydrogen and oxygen. $2H_2O \rightarrow 2H_2 + O_2$. The function of $Ba(OH)_2$ is to increase the conductivity of the solution. Hydrogen thus liberated is liable to contain a trace of oxygen as impurity. In order to make hydrogen free from this impurity, the gas is passed through a bulb containing heated platinised asbestos. Here, oxygen is converted into water. To remove moisture, the gas is successively passed through tubes containing pieces of caustic potash and phosphorus pentoxide. Pure hydrogen is then collected by the downward displacement of mercury.

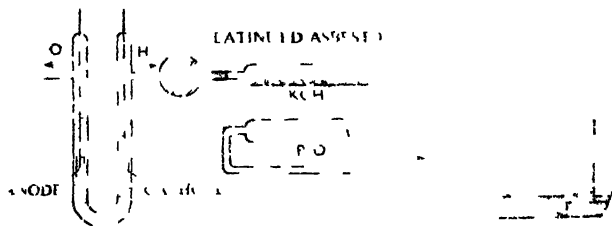


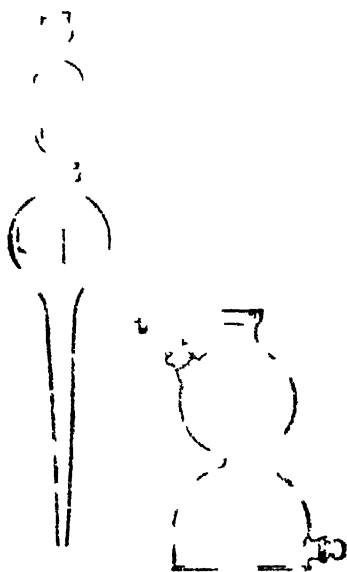
Fig 2(9) Preparation of very pure hydrogen

Preparation of hydrogen in the Kipp's apparatus.

When a steady supply of hydrogen is required for occasional use it is conveniently prepared in a Kipp's apparatus. The advantage of using the apparatus is that the evolution of hydrogen can be regulated according to the necessity.

The Kipp's apparatus consists of two parts which are easily detachable.

The upper part is a glass globe provided with a long conical stem (A). The lower part (B) consists of two globes connected together by a narrow neck. The lowest one appears to be a half globe and is flattened at the bottom so that it may rest on a plane surface. It has an outlet closed by a stopper to drain off the waste liquid from time to time. The upper globe fits air-tight by means of ground glass joint into the neck of the second or central globe while its stem reaches nearly the bottom of the lowest globe. An exit tube with a stop cock is introduced into the central globe by means of rubber stopper. Hydrogen is generated in the central globe and is allowed to escape through the exit tube when required.



A
Fig. 2(10A) Part (A) of the
Kipp's apparatus



B
Fig. 2(10B) Part (B) of the
Kipp's apparatus

For the preparation of hydrogen, pieces of granulated zinc are taken in the central globe. The stop cock is kept open and sufficient quantity of cold, dilute sulphuric acid is poured in through a safety thistle funnel down the upper globe until the acid fills the lowermost globe and comes in contact with zinc in the central globe. The reaction between zinc and dil. acid starts immediately. Hydrogen evolved passes out through the exit tube.

When the stop-cock is closed, the evolved hydrogen cannot pass out and collects in the central globe. The accumulated gas then

exerts a pressure on the acid and pushes it down into the lowermost globe. Then the acid rises up the stem and goes into the uppermost globe and loses its contact with the zinc. The reaction ceases and the evolution of hydrogen stops.

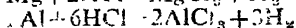
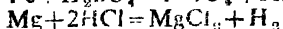
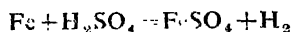
On opening the stop cock again, the gas collected in the central globe escapes through the exit tube and the pressure on the acid is released. As a result, the acid from the uppermost globe flows down through the stem, enters the central globe and reacts with zinc again, yielding a fresh supply of hydrogen.

Thus, when the gas is required, the stop-cock attached to the central globe is kept open. The same is kept closed when the gas is not needed.

N.B. This apparatus is a device used to prepare a gas at the ordinary temperature by the action of a liquid upon a solid.

During the preparation of hydrogen in the Woulfe's bottle, the granulated zinc always remains in contact with the dil. acid and unless one of the reacting substances is eliminated due to the reaction, hydrogen continues to be evolved. Here, the evolution of the gas cannot be controlled as and when required.

(B) In addition to zinc, other metals like iron, magnesium etc. react with dil. hydrochloric acid or dil. sulphuric acid to liberate hydrogen. In fact, all the metals (with the exception of lead) above hydrogen in the electrochemical series (fig 2.11) can liberate hydrogen from acids. The extent to which a given metal will react with a dil. mineral acid to produce hydrogen depends, among other factors, on the position of the metal in the series. The higher the position of the metal, the more vigorous is the liberation of hydrogen.



(with conc. and hot. HCl)

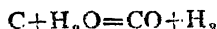
K
Na
Ca
Mg
Al
Zn
Fe
Pb
(H)
Cu
Hg
Ag

Fig 2 (11)

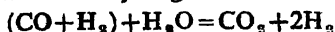
Sodium and potassium are never used to prepare hydrogen from a mineral acid as the reactions are extremely vigorous.

(2) Hydrogen from water :

(A) **Action of steam on coke :** When steam is passed over a bed of white hot coke heated to 1000°C, a mixture containing nearly equal volumes of hydrogen and carbon monoxide is obtained. This gas-mixture is known as water gas.



By removing carbon monoxide from the mixture, hydrogen can be obtained. Water gas is now mixed with excess of steam and is passed at 400°C over the heated catalyst, ferric oxide mixed with chromium oxide (promoter). Carbon monoxide is oxidised into carbon dioxide and more hydrogen is set free from steam.



The mixture of carbon dioxide, hydrogen and a little unreacted carbon monoxide is next passed under high pressure successively through water, caustic potash and ammoniacal cuprous formate solution.

Carbon dioxide is removed by water and caustic potash and carbon monoxide is absorbed by ammoniacal cuprous formate solution. This process of preparing hydrogen from the water gas is called **Bosch process**. This is a method used in commercial preparation of hydrogen.

(B) **Action of metals on water** : Very active metals like sodium, potassium, calcium etc. decompose water giving hydrogen and the hydroxide of the metals. The reaction of water with sodium or potassium is very violent and often takes place with explosion. Metallic calcium reacts with water comparatively slowly, sodium amalgam also decomposes water but with less vigour. The metals which occupy the higher positions in the electrochemical series decompose cold water liberating hydrogen.

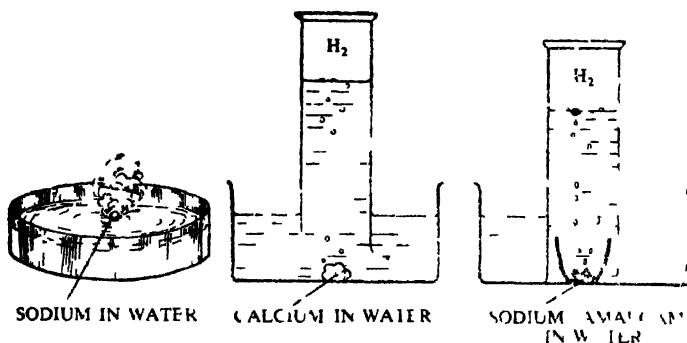
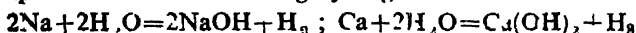
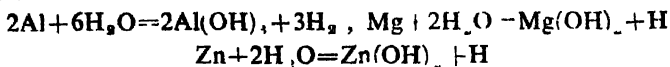
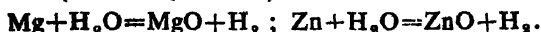


Fig. 2(12)

Powdered aluminium and magnesium as well as their amalgams, zinc copper couple (zinc covered with a layer of copper) decompose boiling water yielding hydrogen and the corresponding hydroxides of the metals.



Strongly heated magnesium or zinc decomposes steam with the evolution of hydrogen. At the elevated temperature, the oxide of the metal (not the hydroxide) is formed.



When super-heated steam is passed over red hot iron (600—

300°C), steam is decomposed to liberate hydrogen. The other product is ferroso ferric oxide or tri iron tetroxide.



This reaction is applied in industrial preparation of hydrogen and the process is known as Lane process.

The iron oxide obtained in the industrial method is reduced by water gas into metallic iron which can decompose further quantity of steam.

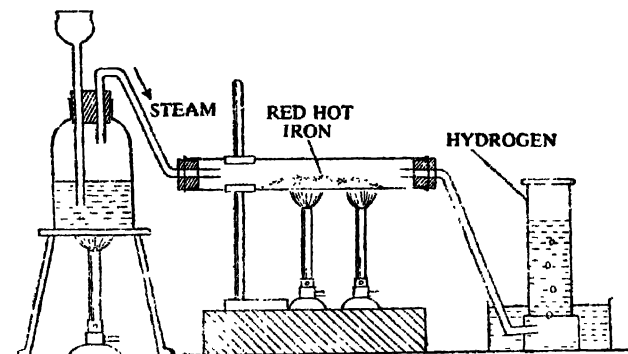
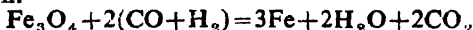
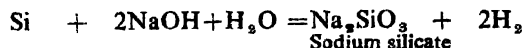
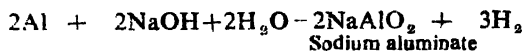


Fig. 2(13) Steam-iron process

This method is rarely used nowadays.

(c) **By electrolysis of water :** An aqueous solution of sodium hydroxide (20%) on electrolysis (using iron sheet as cathode and nickel plated iron sheet as anode), liberates hydrogen at the cathode. A large quantity of hydrogen is obtained as a bye-product when dilute solution of common salt is electrolysed.

(3) **Hydrogen from alkalis :** Hydrogen may be obtained by heating the powdered metals like zinc, aluminium and non-metal like silicon with concentrated caustic soda or caustic potash solution.

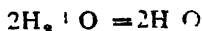


Preparation of hydrogen by reaction between silicon and caustic alkalis is known as the *silicol process*.

Properties—Physical : (i) Hydrogen is a colourless, odourless, tasteless, neutral gas. (ii) It is the lightest gas known. (iii) It is almost insoluble in water. (iv) The gaseous hydrogen can be

condensed to a liquid with much difficulty under very high pressure and at a low temperature (v) It is readily absorbed by metallic palladium

Chemical : (i) Hydrogen is an inflammable gas but is a non-supporter of combustion of other substances. It burns in oxygen or air with a pale blue non-luminous flame producing water



For this reaction, it is rather a source of a fer-product

(2) Under suitable conditions, hydrogen combines with many non-metals forming gaseous or volatile hydrides

Hydrogen does not react with chlorine in the darkness. But when a mixture of hydrogen and chlorine is kept in a light or heated, a violent reaction takes place with the formation of hydrogen chloride $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$

Hydrogen on being heated with bromine yields hydrogen bromide. Hydrogen and iodine unite together in presence of a catalyst producing hydrogen iodide $\text{H}_2 + \text{Br}_2 = 2\text{HBr}$, $\text{H}_2 + \text{I}_2 = 2\text{HI}$

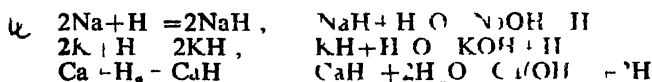
When hydrogen is passed through molten sulphur gas is hydrogen sulphide is given off $\text{H}_2 + \text{S} = \text{H}_2\text{S}$

Under high pressure (200 atm) and temperature (550°C) hydrogen combines with nitrogen in presence of iron as a catalyst to produce ammonia $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$

When subjected to electric spark hydrogen and carbon combine to give a hydrocarbon named acetylene $2\text{C} + \text{H}_2 = \text{C}_2\text{H}_2$

(3) Hydrogen combines with some strongly electropositive metals forming salt-like hydrides

On passing hydrogen over heated metallic sodium, potassium and calcium sodium hydride, potassium hydride and calcium hydride are respectively obtained. Calcium hydride is called *hydrolith*. These metallic hydrides undergo hydrolysis by water to yield hydrogen and the corresponding metallic hydroxides

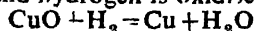


In the above metallic (salt-like) hydrides, hydrogen acts as a reducing agent from the more electropositive metals. In NaH ($\text{Na}^+ \text{H}^-$) hydrogen takes up one electron from sodium whereby sodium is oxidised to Na^+ and hydrogen is reduced to H^- . This is a reaction in which hydrogen causes oxidation

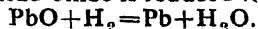
It may be pointed out here that the hydrides of the non-metals mentioned above are all volatile, covalent compounds. Ammonia readily dissolves in water forming an alkaline solution while the aqueous solutions of the hydrides of sulphur, chlorine, bromine and iodine are acidic in character. It will be seen in part II of this book that the element carbon forms innumerable number of hydrides

(4) Due to its affinity for oxygen, hydrogen can act as a reducing agent. By withdrawing oxygen, hydrogen reduces some metallic oxides to the corresponding metals and it itself is oxidised to water.

When hydrogen is passed over heated black cupric oxide, the oxide is converted into dull-red coloured metallic copper. Water is also formed as one of the products. Here, cupric oxide is reduced to the metal and hydrogen is oxidised to water.



Similarly, lead oxide is reduced to metallic lead by hydrogen.



Occlusion of hydrogen : Certain metals such as palladium, platinum, cobalt, nickel etc possess the property of absorbing a large volume of hydrogen gas at the high or even at the ordinary temperature. Of all the metals, palladium absorbs about 900 times its own volume of hydrogen at the ordinary pressure and temperature.

The phenomenon of absorption of hydrogen by a metal is known as occlusion and the absorbed hydrogen as occluded hydrogen. Finely powdered metals can absorb larger volumes of hydrogen. In fact, the occlusion is due to the formation of a solution of gaseous hydrogen in a solid metal. When the metal containing occluded hydrogen is heated, pure hydrogen is given off. This fact is utilised in the purification of hydrogen. Occluded hydrogen is very reactive and is a more powerful reducing agent than ordinary hydrogen. It combines with chlorine or iodine even in the dark while ordinary hydrogen can not do so. When hydrogenised palladium is immersed in a yellow solution of ferric chloride, the latter is readily reduced to a colourless solution of ferrous chloride. But no reaction takes place when a stream of ordinary hydrogen is bubbled through the solution of ferric chloride.

Experiments to prove the important properties of hydrogen :

(1) *Hydrogen is combustible but not a supporter of combustion.*

When a lighted taper is introduced into an inverted gas jar of hydrogen, the taper is extinguished but the hydrogen gas burns steadily at the mouth of the jar with a pale blue flame.

(2) *Hydrogen combines with oxygen violently with explosion :* A hard glass bottle is filled two-thirds with hydrogen and one third with oxygen by displacement of water. Now, the bottle contains a mixture of hydrogen and oxygen in the ratio of 2 : 1 by volume. The mouth of the bottle is carefully closed by a cork. The bottle is then agitated with a towel shaken well. After removing the cork, the mixture is cautiously held before a Bunsen flame when the gases combine instantaneously with a violent explosion and a terrific sound.

(3) *Hydrogen is lighter than air :* (a) A rubber or plastic balloon after filling with hydrogen is tied with a loop of thread and is released in the air. The balloon is found to rise up in the air gradually indicating that hydrogen is lighter than air.



FIG. 2(14)
Burning of hydrogen

- (b) A gas-jar full of hydrogen is held under an 'empty' gas jar (i. e. full of air) and the cover from the mouth of the jar containing hydrogen is removed. After a short while, a lighted taper is inserted into the upper jar when the taper is extinguished but the gas burns at the mouth of the jar with a slight explosion producing a bluish flame. This indicates that hydrogen being lighter than air has left the lower jar and passed upwards displacing the air in the upper jar. A similar test applied to the lower jar will produce no explosion or burning showing that the hydrogen previously in the jar has all been displaced by the air from the upper jar.

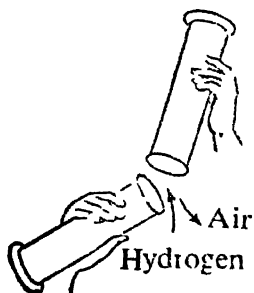


Fig. 2(15) Hydrogen is lighter than air.

- (4) *Hydrogen burns in air or oxygen to produce water.* Hydrogen generated in a Kipp's apparatus is passed through one limb of a U-tube containing anhydrous calcium chloride and the moisture-free gas is burnt at the end of a jet attached to the other limb of the U-tube. The blue flame thus produced is allowed to impinge upon the outer surface of a retort kept cooled by circulating cold water through it. It is found that drops of colourless liquid form on the cooled surface of the retort and collect inside a beaker kept below it. The liquid turns anhydrous, colourless copper sulphate blue, indicating that the liquid is water. Here, hydrogen burns in oxygen of the air producing steam which condenses to liquid water at the cold surface of the retort. $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$.

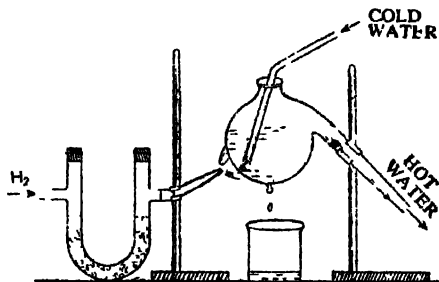


Fig. 2(16) Formation of water by burning hydrogen in air

It is to be noted that perfectly dry hydrogen and oxygen do not combine. So this experiment is to be performed with gases containing traces of moisture.

- (5) *As a result of reaction between hydrogen and chlorine, hydrogen chloride is produced.* When a burning jet of hydrogen is introduced into a gas-jar of chlorine, hydrogen continues to burn giving off white fumes of hydrogen chloride. A little water is then poured into the jar and shaken well. To a portion of the solution, silver nitrate solution is added when a curdy white precipitate is obtained. The precipitate is insoluble in conc. nitric acid but readily soluble

in ammonium hydroxide. This test indicates the presence of HCl in the solution obtained by dissolving the white fumes in water.

(6) *Hydrogen possesses reducing properties.*

A small quantity of pure, black cupric oxide is taken in a hard glass combustion tube clamped in a horizontal position. An inlet tube is connected to one end of the tube. A small bulb tube attached to the other end serves as the outlet tube. A slow stream of dry and pure hydrogen is passed through the inlet tube while the combustion tube containing cupric oxide is strongly heated. After some time, it is found that a dull red-coloured solid is left in the tube instead of the

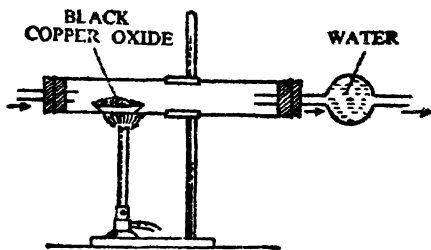


FIG. 2(17) Reduction of cupric oxide by hydrogen

black oxide and drops of a colourless liquid appear in the outlet tube on cooling. The red solid dissolves in conc. nitric acid giving a blue solution. A dark brown gas is evolved at the same time. The solid is thus proved to be the metallic copper. The liquid in the outlet tube is water as it turns anhydrous, colourless copper sulphate blue. $\text{CuO} + \text{H}_2 = \text{Cu} + \text{H}_2\text{O}$

The above experiment illustrates that hydrogen at a high temperature reduces cupric oxide to metallic copper and is itself oxidised to water.

Uses of hydrogen : (1) Hydrogen being the lightest gas known is used for filling balloons and airships. But due to its inflammability, the use in this respect is extremely limited. (2) It is used in the production of oxy-hydrogen flame (temp. 2000°C) required in cutting and welding purposes and in lime light. (3) Large quantities of hydrogen are used in the manufacture of ammonia, hydrochloric acid and methyl alcohol. (4) Nowadays, hydrogen finds its application in the conversion of coal to synthetic petrol. (5) The gas in huge quantities is used for hardening of vegetable and animal oils. (6) It is sometimes used in the laboratory as a reducing agent.

Tests : (a) The gas is identified by igniting it in air or oxygen when it burns with a pale blue flame. The product of combustion of the gas in oxygen is water which turns white, anhydrous copper sulphate blue. (b) the gas is absorbed (occluded) by spongy palladium metal and is set free again when the hydrogenised metal is heated.

Nascent hydrogen : An element is said to be in the *nascent state* (meaning new-born condition) when it is just liberated in a chemical reaction. Thus hydrogen at the moment of its generation or birth from a compound is called *nascent hydrogen*.

Allotropy of hydrogen—Ortho and Para hydrogen : A hydrogen molecule is diatomic. Each of the two hydrogen atoms constituting a molecule has a single electron which rotates about a proton in the nucleus. In other words it may be said that a hydrogen molecule consists of two protons and two electrons.

In 1927, Heisenberg predicted the possibility of existence of two kinds of hydrogen molecule. According to him, the proton in the nucleus of a hydrogen atom is spinning like a top and the two protons in the hydrogen molecule may spin either in the same (parallel) or opposite sense. When the spin of the two protons is in the same direction, this form of hydrogen is known as *ortho hydrogen* and the other form with the spin of the two protons in



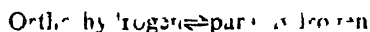
Ortho hydrogen

Para hydrogen

Fig. 2 (18)

opposite direction is called *para hydrogen*. These forms are considered as two *allotropic forms* of hydrogen. In 1929, Bonhoeffer and Harteck successfully prepared different varieties of hydrogen by absorbing ordinary hydrogen on wood charcoal at the temperature of liquid air or liquid hydrogen. Thus, the view of Heisenberg was confirmed.

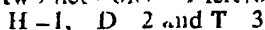
Ordinary hydrogen is an equilibrium mixture of ortho and para hydrogen in the ratio of 3 to 1 at the ordinary temperature.



On lowering the temperature, the proportion of the *ortho* form decreases and that of the *para* form increases.

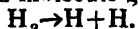
These two allotropic forms are similar in general properties but differ slightly in their specific heat, thermic conductivity etc.

Isotopes of hydrogen Hydrogen has three isotopes—ordinary hydrogen or protium H, heavy hydrogen or deuterium D, and tritium T. All these have one extra nuclear electron per unit. In ordinary hydrogen, the nucleus consists of one proton. In deuterium, the nucleus contains one proton and one neutron. In tritium it contains one proton and two neutrons. Therefore the atomic masses are—



Position of hydrogen in the periodic table has been given in part II of this book.

Atomic hydrogen It has been shown that at a very high temperature, ordinary hydrogen molecule gets dissociated into atoms.



In the splitting of the hydrogen molecule, a large amount of energy (about 104.2 K cal/gram-molecule) is absorbed. Atomic hydrogen is formed when an electric arc is struck between two tungsten electrodes (1000—2000 C) and a jet of hydrogen is passed through the arc. By applying this method, Langmuir in 1915 prepared it. Atomic hydrogen is chemically very active and possesses strong reducing properties. It is capable of forming hydrides with certain metals and nonmetals at the ordinary temperature. It reacts with chlorine even in the dark and with molecular oxygen to produce hydrogen peroxide. $O_2 + 2H \rightarrow H_2O_2$.

It reduces solutions of silver nitrate, copper nitrate and mercuric chloride to the corresponding metals and carbon monoxide to formaldehyde. $AgNO_3 \rightarrow Ag$; $Cu(NO_3)_2 \rightarrow Cu$
 $HgCl_2 \rightarrow Hg$; $CO + 2H \rightarrow HCHO$.

It can easily reduce the acidified solutions of potassium dichromate to chromic salt and potassium permanganate to manganous salt. These types of reduction cannot be brought about by ordinary hydrogen. Since the conversion of the hydrogen molecule into atoms is a highly endothermic reaction, a large amount of energy will be released during the recombination of hydrogen atoms into molecule. When the atoms produced by the thermal dissociation of the hydrogen molecule come in contact with a metallic surface, they combine immediately producing a temperature between 4000 C and 5000 C.

It must be remembered that in spite of similarities in reactions, atomic hydrogen in the true sense is not the same as nascent hydrogen.

WATER

Formula H_2O	Mol. wt. 18	Vap. density 9	Sp. gr. 1
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Water is of fundamental importance to all plants and animals in maintaining the vital processes necessary to life and growth.

Water for a long time was considered to be an element. It was only in 1781, water was shown to be a compound by Cavendish who obtained it by exploding a mixture of two volumes of inflammable air (hydrogen) and one volume of oxygen. On the basis of the results of several experiments, Lavoisier proved conclusively that water is a compound of hydrogen and oxygen. Water is widely distributed in nature and occupies about three-fourths of the surface of the earth.

According to the source, natural water is mainly divided into four classes.

(1) **Rain water** : Water from the seas, rivers, lakes etc escapes in the air as vapours under the influence of sunrays. The vapours thus produced cool down at the high altitude of the atmosphere and condense to liquid water which returns to the surface of the earth in the form of rains. Thus, rain water may be regarded as naturally distilled water and is taken as the purest form of natural water. Still it is contaminated with many impurities while passing through the atmosphere. For instance, it contains dissolved gases like oxygen,

carbon dioxide, traces of ammonia, nitrous and nitric acids together with suspended dust particles. Rain water in the vicinity of industrial towns also contains traces of sulphurous and sulphuric acids formed as a result of burning of coal containing iron pyrites (FeS_2). The first shower contains the greater portion of the dissolved impurities. Consequently, rain water collected after a few showers is more pure.

(2) **River water :** Rain water and water from the melting of ice on mountains lead to the formation of rivers. Obviously, river water contains all impurities generally present in the rain water. Moreover, it is liable to contain many other impurities both soluble and suspended, organic and inorganic, which a river derives during its passage over the soil and rocks. The amount and kind of impurity will depend, therefore, on the type of soil over which the water runs. Impurities commonly found in river water are the chlorides, sulphates, carbonates, bicarbonates of sodium, calcium, magnesium, iron etc. Besides these, it often carries impurities from the ebbages and sludges of the places through which the river passes. River water is sometimes contaminated with various types of bacteria and is generally turbid due to the presence of large amount of suspended clay particles.

Spring and well water : Rain water falling on the ground makes its way downwards through the porous strata of the soil into the interior of the earth. When the flow of such water is stopped by some impermeable stratum such as granite, hard clay etc., it collects there in the form of well-water which in course of time may rush up to the surface as spring water. This water undergoes natural filtration while passing through various layers of sand, gravels etc. and is free from suspended impurities. It is clear and transparent but contains larger amounts of soluble chlorides, sulphates bicarbonates of calcium, magnesium, sodium, potassium and sometimes iron. Spring water and well water may contain dissolved gases like carbon dioxide, sulphur dioxide, hydrogen sulphide etc. Some of the springs are found to contain water having a temperature much higher than the ordinary temperature. This happens as the hot gases accumulated inside the earth escape through the water of such springs. The hot spring at Sitakunda in India may be mentioned here.

Spring water containing an excessive quantities of soluble mineral and gaseous substances is often referred to as *mineral water*. Due to the presence of various types of salts in solution, this water has a characteristic taste and possesses curative property. Such water contains excess of dissolved carbon dioxide gas, chlorides, sulphates and bicarbonates of metals like sodium, calcium magnesium. Sometimes iron salts, iodides, sulphides etc. are also found present in it. Mineral water is occasionally used for medicinal purposes.

Sea water: Sea water is the reservoir into which all the impurities carried by natural waters eventually go. Hence, the total solid content of sea water is usually high (about 3.6% of which 2.6 is sodium chloride). It contains maximum amount of dissolved salts like chlorides, sulphates, carbonates, bromides, iodides of sodium, potassium, calcium, magnesium. Sea water is unsuitable for drinking purpose due to the presence of large amount of common salt in solution.

Soft water and Hard water Depending upon the behaviour of water towards ordinary soap, natural water is divided into two classes: (a) Soft water and (b) Hard water.

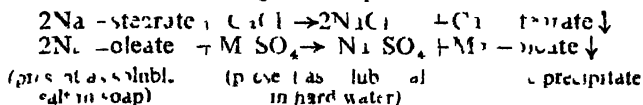
Soft water Water which readily forms lather with soap is called soft water.

Hard water Water which does not readily form a lather with soap and produces the same with difficulty after consuming a sufficient quantity of soap is known as hard water.

Cause of hardness All natural waters contain soluble and the salts as non-volatile impurities and the distinction between hard and soft waters is based on the nature of the dissolved substances present in them. Water containing dissolved bicarbonates and calcium salts is found to be hard. Therefore hardness is due to the presence of soluble calcium and magnesium salts like bicarbonates, sulphates and chlorides of these metallic ions.

Sometimes a sample of water becomes hard after containing a new soluble salt of iron.

Ordinarily, soaps consist of sodium and potassium salts of higher fatty acids like stearic, palmitic, lauric, etc. The soluble metallic salts are soluble in water and the detergent effect of the soap is observed when these salts pass in solution producing lather or foam. On the other hand, the calcium and magnesium salts of these fatty acids are insoluble in water. When a sample of hard water the soap reacts chemically with the soluble calcium, magnesium and iron salts present in the hard water to produce the corresponding salts of these organic acids which appear as insoluble white precipitate. Consequently soap does not give rise to any lather so long as this precipitation goes on to remove all the calcium, magnesium or iron ions. After removal from the hard water. This causes a considerable wastage of soap.



On the basis of the above discussions, the definitions of hard and soft water are given below.

Water that contains dissolved bicarbonates, chlorides and sulphates of calcium, magnesium or iron and is incapable of giving any lather with soap unless all the three metallic ions present in it are removed is regarded as **hard water** and water containing very little or no calcium, magnesium or iron salts and so capable of producing lather easily with soap is known as **soft water**.

Types of hardness : Hardness of water is of two types—(a) Temporary hardness and (b) permanent hardness.

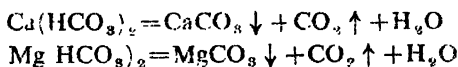
Hardness which is due to the presence of dissolved bicarbonates of calcium, magnesium (sometimes iron) in water is called **temporary hardness** and water having this type of hardness is known as temporarily hard water. This hardness is termed temporary because it can be removed by easy means like boiling and sedimentation.

On the other hand, hardness which is due to the presence of dissolved chlorides and sulphates of calcium, magnesium (or iron) in water is called **permanent hardness**. This hardness is characterised as permanent, for it cannot be removed by mere boiling or by any other easy means. Water possessing this type of hardness is referred to as permanently hard water.

Removal of hardness—softening of hard water : If the soluble bicarbonates, chlorides sulphates of calcium and magnesium (or iron) present in water are converted into insoluble substances by simple boiling or by using chemical reagents and removed as precipitates, the water that remains is soft. Almost all the methods of removing a hard water soft are primary based on this principle.

Softening of temporary hard water : Temporary hardness can be removed by either (a) boiling or (b) Clark's process using lime.

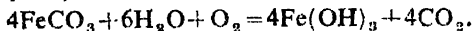
✓ (a) **By boiling :** On boiling, the soluble bicarbonates of calcium, magnesium (and iron) present in temporarily hard water decompose producing insoluble carbonates which are precipitated. The precipitates are allowed to settle down and the soft water is collected from above.



As a result of boiling, ferrous bicarbonate if present decomposes similarly.



Since ferrous carbonate is readily oxidised by atmospheric oxygen, a precipitate of ferric hydroxide is obtained.

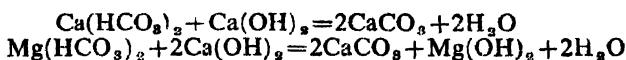


It is to be noted that magnesium carbonate is soluble in water to an appreciable extent. So the hardness which is due to the presence of magnesium bicarbonate cannot be completely removed by simple boiling.

This method is not suitable for softening temporarily hard water on a large scale.

✓ (b) **Clark's process :** By this process, temporary hardness is removed by the addition of requisite quantity of slaked lime which reacts with the soluble bicarbonates of calcium and magnesium. Calcium bicarbonate is thrown down as insoluble precipitate of calcium carbonate and magnesium bicarbonate as very slightly soluble magnesium hydroxide.

The precipitates formed can be removed by filtration through beds of coke or sand.



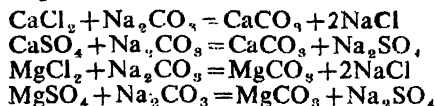
Only calculated amount of lime must be used. If more than the requisite quantity of lime is added, the excess goes into the solution. As a result, free Ca^{++} ions enter into water and the water becomes hard again.

In the case of magnesium bicarbonate hardness, double the amount of lime is added in order to precipitate magnesium hydroxide.

When the magnesium content is high, addition of milk of lime along with sodium carbonate is preferred in precipitating magnesium hydroxide.

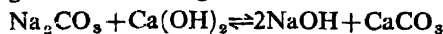
Softening of permanently hard water : Permanently hard water is usually softened by treatment with washing soda or sodium carbonate (soda process). Simultaneous removal of both temporary and permanent hardness of water is effected by addition of soda mixed with lime (lime soda process) or by the permutit process.

Soda process : Permanent hardness of water can easily be removed by adding washing soda or sodium carbonate to it when soluble chlorides and sulphates of calcium and magnesium are converted into the insoluble carbonates of the corresponding metals and are precipitated. On removing the insoluble carbonates by filtration through a filter-press, soft water is obtained.

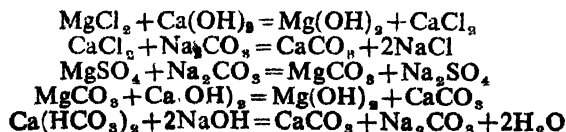


Sodium salts formed pass into the solution but these salts are innocuous with regard to soap.

Lime soda process : On a commercial scale, lime soda process is used to remove both types of hardness (temporary and permanent) of water. In this process, hard water is treated with a mixture of calculated amount of slaked lime and sodium carbonate known as the lime soda mixture. The constituents of the mixture interact according to the following reversible reaction :



So, Na_2CO_3 , $\text{Ca}(\text{OH})_2$ and NaOH are available to precipitate Ca^{++} and Mg^{++} ions from the hard water. The dissolved calcium salts are precipitated as calcium carbonate and the magnesium salts as the hydroxide. In order to facilitate precipitation, a little sodium hydroxide is sometimes added.



Soft water is obtained by filtering the precipitated carbonates and the hydroxides through a filter-bed. This process is a costly one.

✓ **Permutit process.** To soften a large quantity of hard water, this method is nowadays widely used. By this process, both temporary and permanent hardness of water can be eliminated at the same time.

According to the name of its discoverer, this method is sometimes referred to as Gan's process.

There are some naturally occurring minerals called zeolites. These are complex substances consisting of mixtures of sodium and aluminium silicates. The zeolites are insoluble in water. The permutit is the commercial name for artificially prepared sodium aluminium silicate allied to the zeolites found in nature. The remarkable property by virtue of which the permutit is used as a water-softener is that it can exchange its sodium with other metals when brought in contact with the solutions containing those metals.

The permutit water-softening plant consists of a vertical cylindrical vessel made of bricks or iron and contains a bed of sodium permutit between layers of gravel and sand. The hard water is allowed

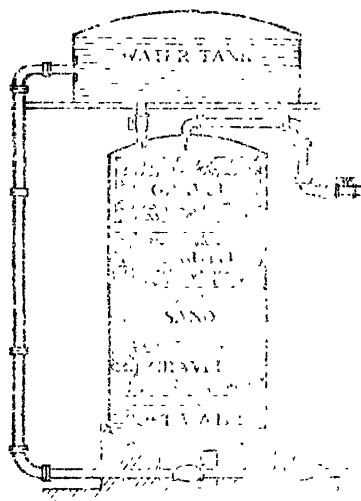


FIG. 2(19) Permutit process of softening water on a large scale

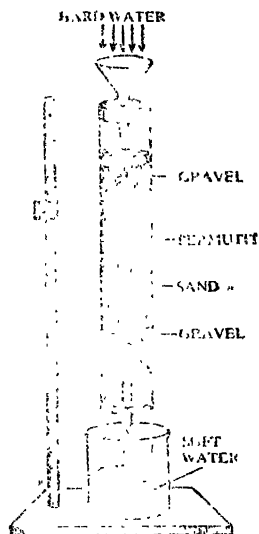
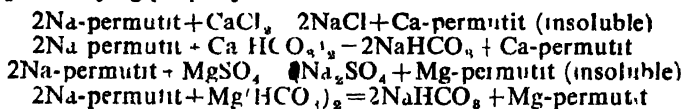


FIG. 2(19A) Permutit filter for domestic use

to pass through the bed when base exchange occurs. The sodium permutit reacts with the soluble calcium and magnesium salts

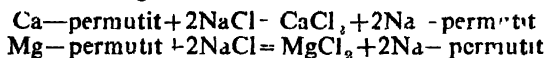
present in hard water producing insoluble calcium and magnesium permutits which are precipitated and retained in the bed. The filtered water coming out through the outlet at the bottom is soft and perfectly free from any calcium and magnesium salts having soap-destroying property.



This method is also called *base exchange* or *zeolite process*. The permutit water-softener is also used to get soft water required for domestic purpose.

Due to long use, the permutit loses its ability to soften water as all the sodium present in it is spent up to form calcium and magnesium compounds.

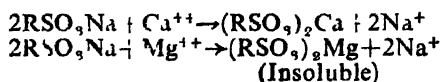
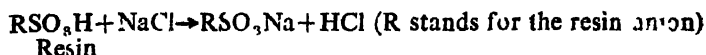
This ineffective bed of permutit can be re-activated by passing a strong solution of sodium chloride (10%) through it. This treatment causes replacement of calcium and magnesium from the exhausted permutit by sodium of the sodium chloride. Thus, the original sodium permutit is regenerated in the bed which can be used again.



The chlorides of calcium and magnesium are washed away.

Ion-exchange resins as water softeners : Some synthetic organic substances known as ion-exchange resins are now increasingly used for water-softening. These are complex substances each of which contains a sulphonic acid ($-\text{SO}_3\text{H}$) group. They are more active and efficient than permutit. The hydrogen atom of the $-\text{SO}_3\text{H}$ group can be replaced by metals to produce salts.

The resin is first converted into its sodium compound by treatment with sodium chloride solution, when the hydrogen ion of the sulphonic acid group is exchanged for sodium ion. The resin in the form of Na-compound is used as a water softener. When hard water is allowed to percolate through a layer of the sodium resin, all the calcium and magnesium ions present in water are replaced by Na^+ ions of the resin. The issuing water is now free from Ca^{++} or Mg^{++} ions and is soft.



The resin after being used for a long time loses its activity like the permutit and is revived by treatment with a solution of sodium chloride.

Sodium hexametaphosphate (NaPO_3)₆ under the trade name *calgon* is employed as a water softener which removes the calcium hardness by forming a soluble complex salt.

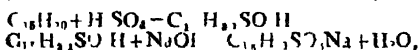
Hard water may also be softened by means of E. D. T. A. (Ethylene diamine tetra acetate) which removes Ca^{++} and Mg^{++} ions present in water by forming soluble complexes.

Estimation of hardness The hardness of water also called the soap destroying or soap-precipitating power of water depends on the amounts of the dissolved calcium, magnesium or iron salts in it and is expressed in degrees. If a sample of water contains n parts of CaCO_3 or its equivalent per million parts (ppm), it has n degrees of hardness. So, each degree of hardness represents the hardness produced by 1 part of calcium carbonate (or its equivalent) in 1,000,000 parts of water. The degrees of hardness of a sample of water containing 50 parts by weight of MgSO_4 per 1,000,000 parts of it is to be expressed as follows:

$$\begin{aligned} 50 \text{ parts of } \text{MgSO}_4 &= 50 \text{ parts of } \text{CaCO}_3 \\ \therefore \text{Degrees of hardness} &= 50 \text{ ppm or parts per million} \end{aligned}$$

Total hardness of water is usually estimated by titration of a measured volume of water with a soap solution which is previously standardised against water containing a known concentration of calcium chloride. The end point of titration is arrived at when the standard soap solution gives a lather lasting for 1–2 minutes on shaking. The permanent hardness is estimated by similar titration of same volume of water after removing its temporary hardness by boiling. The difference between the two results denotes the temporary hardness.

Synthetic detergents have now been introduced to replace soap in domestic and industrial work. A typical detergent is a reduced long complex hydrocarbon of the type $\text{C}_n\text{H}_{2n+1}$ where n is greater than 12. The hydrocarbon is first treated with concentrated sulphuric acid whereby a $-\text{SO}_3\text{H}$ group is introduced into the molecule of the hydrocarbon. This is then converted into its sodium salt by means of sodium hydroxide solution, the sodium salt is the detergent.



A detergent has two advantages over soap: it is more soluble in water. It is not affected by hard water as the calcium or magnesium salt of the detergent is soluble in water.

Numerical problems on hardness of water :

(1) One litre of a sample of hard water contains 1 mg of CaCl_2 and 1 mg of MgCl_2 . Find the total hardness in terms of parts of CaCO_3 per 10^6 parts of water by weight.

$$\begin{aligned} \text{Mol. wt. of } \text{CaCl}_2 &= 40 + 2 \times 35 = 111 \\ \text{Mol. wt. of } \text{MgCl}_2 &= 24 + 2 \times 35 = 95 \\ \text{Mol. wt. of } \text{CaCO}_3 &= 40 + 12 + 48 = 100 \\ \therefore 111 \text{ gm. of } \text{CaCl}_2 &\approx 100 \text{ gm. of } \text{CaCO}_3 \\ \therefore 1 \text{ gm. of } \text{CaCl}_2 &\approx \frac{100}{111} \text{ gm. of } \text{CaCO}_3 = 0.90 \text{ gm. of } \text{CaCO}_3 \\ \therefore 1 \text{ mg. of } \text{CaCl}_2 &= 0.9 \text{ mg. of } \text{CaCO}_3 \end{aligned}$$

Again, 95 gm of $\text{MgCl}_2 \equiv 100 \text{ gm of } \text{CaCO}_3$

$\therefore 1 \text{ gm of } \text{MgCl}_2 \equiv \frac{100}{95} \text{ gms of } \text{MgCl}_2 \equiv 1.05 \text{ gms of } \text{MgCl}_2$

$\therefore 1 \text{ mg } \text{MgCl}_2 \equiv 1.05 \text{ mg } \text{CaCO}_3$.

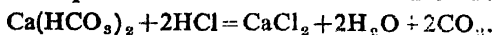
i.e. 1 litre of the hard water contains $(0.9 + 1.05) = 1.95 \text{ mg of } \text{CaCO}_3$

1 litre of water = 1000 gms or 10^6 mg of water .

\therefore The hard water contains 1.95 parts of CaCO_3 per 10^6 parts of water by weight.

(2) 100 ml of tap water containing CaHCO_3 was titrated with N/50 HCl with methyl orange as indicator. If 30 ml of HCl were required, calculate the temporary hardness as parts of CaCO_3 per 100,000 parts of water.

The equation of the reaction between CaHCO_3 and HCl is



Mol wt. of $\text{CaCO}_3 = 40 + 12 + 48 = 100$

Again, CaCO_3 (100 parts) + CO_2 + $\text{H}_2\text{O} = \text{Ca}(\text{HCO}_3)_2$

$\therefore 2 \text{ equivalents of HCl} \equiv 1 \text{ eq. } \text{Ca}(\text{HCO}_3)_2 \equiv 1 \text{ eq. } \text{CaCO}_3$

$\therefore 1 \text{ eq. of the acid} \equiv 50 \text{ parts of } \text{CaCO}_3$

i.e. 1000 ml of the (N) acid $\equiv 50 \text{ gms of } \text{CaCO}_3$

or, 1 ml of (N) acid $\equiv 0.05 \text{ gm of } \text{CaCO}_3$

100 ml of tap water $\equiv 30 \text{ ml } \frac{\text{N}}{50} \text{ HCl} \equiv 30, 50 \text{ ml (N) HCl}$

$$= \frac{30}{50} \times 0.05 \text{ or } 0.03 \text{ gm } \text{CaCO}_3$$

\therefore 100,000 ml (or 100,000 gms) of tap water contain 30 gms of CaCO_3

\therefore Tap water contain 30 parts of CaCO_3 per 100,000 parts of water.

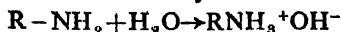
De-ionisation of water or de-mineralised water :

Water softened by the permutit or any other similar process is never free from soluble mineral matters. During removal of Ca^{++} and Mg^{++} ions which are responsible for the hardness, Na^+ ions are introduced into the water in amounts equivalent to the ions removed.

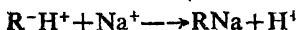
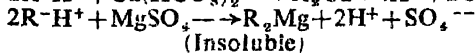
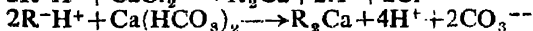
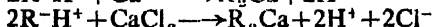
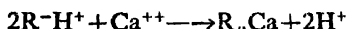
Nowadays, water is demineralised or made free from all electrolytes by passing it in succession through two different types of organic resins called ion-exchange resins. This process of removing all cations and anions of the dissolved electrolytic impurities in water is called *de-ionisation* or *de-mineralisation of water*.

The resins which are employed to remove the cations or positive ions are known as the cation exchangers while the resins used to remove the anions or the negative ions are designated as the anion exchangers. These resins are complex, synthetic, insoluble organic substances. The cation exchange resins contain H^+ ions derived usually from $-\text{COOH}$ or SO_3H groups present in their molecules. For the sake of brevity, we represent these types as R-H^+ . The

anion exchange resins are also organic amino ($-\text{NH}_2$) compounds of high molecular weight. These resins in contact with water yield substituted ammonium hydroxide compounds.



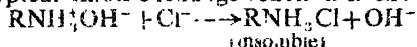
The process of deionisation consists of two stages. In the first stage, the water containing soluble salts is passed through a bed of cation exchanger kept in a suitable tank. All cations like Ca^{++} , Mg^{++} , Na^+ etc. present in water are exchanged for H^+ ions in the resins and are removed. The water becomes distinctly acidic as equivalent amounts of H^+ ions are introduced into it.



The water after this treatment is free from all metallic ions but it contains H^+ ions as only cation and anions like Cl^- , SO_4^{--} , CO_3^{--} etc.

In the second stage, the acidic water coming out of the cation exchanger is passed through another bed of organic resins of opposite character i.e. anion exchanger. Here, all the anions present in water are exchanged for $-\text{OH}$ ions of the resins and are trapped on the resins.

A typical anion exchange reaction is shown below.



All other anions are removed similarly.

The OH^- ions liberated neutralise the H^+ ions set free in the first stage producing water $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$.

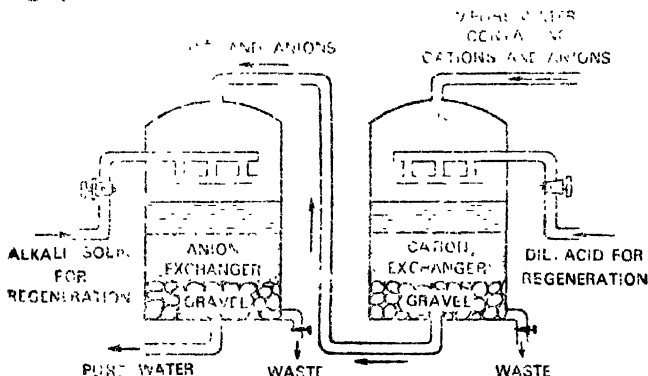


Fig. 2(20) De-mineralisation or softening of water by using cation and anion exchangers in succession

The effluent from the anion exchanger is neutral water which does not contain any mineral matter or ions. This water is as pure as distilled water. So by percolating through ion exchange resins, we can obtain water of the quality of distilled water without distillation.

The cation exchanger when exhausted due to prolonged use can be regenerated by treating it with dilute sulphuric acid and the used up anion exchanger is similarly re-activated by treatment with a dilute solution of sodium hydroxide. The resin beds are thus made ready for use again.

Both the permutit process and the ion exchange process soften water by exchanging of ions. The permutit process exchanges the M^{++} (Ca^{++} and Mg^{++}) ions responsible for the hardness with Na^{+} ions while the ion exchange process exchanges these ions with H^{+} ions. If permutit is exhausted, it is regenerated by treating it with a dilute solution of sodium carbonate. The ion exchange process using water compatible Organic ion exchange resins can be used continuously and an ion exchanger yields water practically free from any ion.

Uses of water. Water is used for both domestic and industrial purposes. (1) Its use for drinking and cooking purposes is indispensable. (2) For washing clothes and other materials, the quantity of water is required. (3) Water is used in the home. (4) In industries, water is mainly used in the steam boilers. Much water is consumed by the chemical and other factories. (5) In the laboratories, it is primarily used for washing. (6) Besides water finds its application in storing, heating, cooling, and medicinal preparations.

Water is purified by application of different methods according to the nature of its use.

Water can extinguish most fire. Petroleum, the kerosene, petrol, fire, Petrol is lighter than water and it floats on the surface of water and catches fire.

Disadvantages of using hard water

(1) For washing clothes and garments with hard water is not suitable. With hard water no detergent effect of soap is observed unless a large amount of it is consumed to remove the dissolved calcium and magnesium salts in the form of curdy soap precipitates. To prevent wastage of soap, hard water must be softened when used for laundry purposes. Presence of iron salts in laundry water is objectionable because it is easily oxidised to the ferric state which causes brown or similar stains on fabrics.

(2) If water containing calcium and magnesium bicarbonates is heated in a kettle for a long time, the inside of the latter becomes covered with a layer of insoluble calcium and magnesium carbonates formed by the decomposition of the bicarbonates of the metals. This layer is a non-conductor of heat and it becomes difficult to boil water in such a container.

(3) In industries, water that is used for raising steam in boilers must be rendered soft as otherwise when the water is evaporated off, a deposit of solid calcium carbonate, magnesium carbonate and calcium sulphate is formed on the inside walls of the boilers. This hard and heat-insulating deposit known as 'boiler scale' causes greater consumption of fuel for heating water in a boiler and also causes rapid deterioration of the boiler plates through overheating. Sometimes, an unequal expansion of the boiler and its scale takes place due to continued heating and the boiler bursts with explosion.

It is to be noted that when water containing magnesium chloride is heated in a boiler, the salt undergoes hydrolysis giving magnesium oxychloride and hydrochloric acid. The acid attacks the boiler and shortens its life. Magnesium oxychloride becomes a part to the deposited boiler scale. $\text{MgCl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{Mg}(\text{OH})\text{Cl}$.

For drinking purpose, water of zero hardness is not preferred. Small quantities of dissolved calcium salts are essential for the growth of human body.

Drinking or potable water : Drinking water should be clear, colourless and of a refreshing taste which is imparted by the dissolved salts present in it. It must be free from disease-producing germs and other suspended materials injurious to health. It must not contain dissolved copper or lead compounds which are cumulative poisons and in no way it should contain excess of common salt. Water containing nitrates to a common is unsuitable for drinking purposes as the presence of this substance in water indicates contamination with sewage and decaying animal or vegetable matter. However, drinking water need not be filtered or chemically purified. On the other hand, very small quantities of dissolved sodium, potassium, magnesium, calcium salts and carbon dioxide give water its pleasant taste and are necessary for growth of living organisms. The process of purification of natural water for drinking purpose may be divided into three main heads—
(a) Removal of suspended impurities, (b) Steps to kill the pathogenic bacteria.

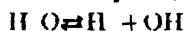
In cities and towns, water from a river, canal or a lake is pumped up and stored in tanks where the suspended particles settle down slowly. Potash alum is added for quick coagulation of the suspended matters and hastening the settling process. Aluminium hydroxide precipitated as a result of the reactions carries down suspended heavy particles of clay and some bacteria. This water is then run from the top into filter beds consisting of three layers—the upper layer of fine sand, the middle layer of coarse sand and the bottom layer of graded gravel. Filtered water is taken out through the drains below the gravel layer and is collected in big reservoirs. After a few days, the fine sand filter becomes covered with a slimy layer of clay, algae, etc. which acts as a filtering medium and holds up the suspended impurities and the bacteria.

Water thus filtered is subjected to sterilisation. Some of the important sterilising agents used are liquid chlorine, bleaching powder, ozonised air, potassium permanganate etc. In recent times, water is often freed from bacteria by a short exposure to ultra violet rays.

Preparation of chemically pure water Water free from suspended or non-volatile, soluble, impurities is obtained by distillation. Water required for chemical work is usually prepared by distilling it from a copper or an iron vessel provided with a copper condenser and by collecting the middle portion of the distillate. This water is not perfectly pure. It may be contaminated with dissolved gases. By passing chlorine through the boiling distilled water, nitrogenous organic compounds are usually removed. The excess of chlorine is then driven off by boiling.

This purified water can be converted to extra pure water by re-distilling it in presence of potassium permanganate and caustic potash. The distillation is carried out in an apparatus made of pyrex glass.

Properties of water - Physical (1) Pure water is odourless, tasteless, clear and colourless liquid at ordinary temperature. It then layers itself into less dense clear bluish layer (bottom) and thicker (0°C to 4°C) when it becomes more dense (4°C to 0°C). Above and below 4°C it is less dense. (2) Water in the pure condition is a very poor conductor of electricity. It ionises very slightly into hydrogen and hydroxyl ions.



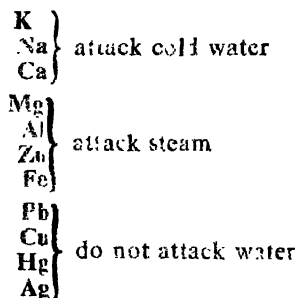
But its electrical conductivity increases to a considerable extent by the addition of a small amount of an acid or alkali. (3) Water is a good solvent having the power of dissolving many substances either at ordinary temperature or high temperature. Conc. sulphuric acid, caustic soda, caustic potash dissolve in water with evolution of much heat while heat is absorbed during the preparation of a solution of ammonium chloride in water.

Chemical (1) Water is a *neutral* liquid to litmus. (2) It is a good *ionising solvent*. Electrolytes like acids, bases and salts dissolve in water and dissociate into ions.

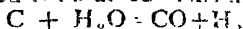
(3) In many chemical reactions, water acts as a *positive catalyst*. Perfectly dry hydrogen and chlorine do not react at all, but in presence of a trace of moisture, the combination takes place with the formation of hydrogen chloride. (Phosphorus and sulphur do not burn in pure and dry oxygen even at high temperature, but they burn vigorously in oxygen containing a little moisture.)

(4) **Action of water on metals** The action of water on metals to yield hydrogen has been fully described in page 20. It can be

shown that water attacks the metals to a degree varying with their positions in the electrochemical series.



(5) *Action on non-metals* : When steam is passed over white hot coke. (at about 1000 C) a mixture of equal volumes of carbon monoxide and hydrogen is obtained. This mixture is known as water gas.

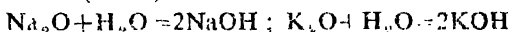


Similarly, silicon at white heat, decomposes water forming hydrogen and silica dioxide $\text{Si} + 2\text{H}_2\text{O} = \text{SiO}_2 + 2\text{H}_2$.

Chlorine reacts with cold water giving a light yellow solution called chlorine-water which contains hydrochloric acid and hypochlorous acid. $\text{Cl}_2 + \text{H}_2\text{O} = \text{HCl} + \text{HOCl}$.

In bright sunlight, water is decomposed by chlorine forming hydrochloric acid and oxygen. $2\text{Cl}_2 + 2\text{H}_2\text{O} = 4\text{HCl} + \text{O}_2$.

(6) *Action on metallic oxides* : Sodium oxide or potassium oxide reacts with water at the ordinary temperature forming the metallic hydroxide (alkali) in solution.



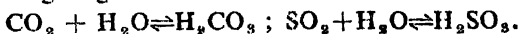
Sodium peroxide, on being reacted with water at the ordinary temperature, evolves oxygen and forms sodium hydroxide which remains in solution. $2\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} = 4\text{NaOH} + \text{O}_2$.

Calcium oxide (quick lime) is attacked by cold water with the formation of slightly soluble calcium hydroxide or slaked lime.

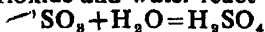


This reaction takes place with a hissing sound and generation of much heat. Lime becomes hot; it commences to swell up and crack and finally crumbles to powder. A portion of water is seen to escape as steam.

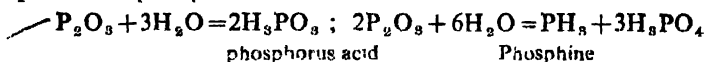
(7) *Action of non-metallic oxides* : Acidic oxides like carbon dioxide and sulphur dioxide dissolve in cold water producing carbonic acid and sulphurous acid respectively. These acids are not stable compounds. On heating the solutions of these acids, the oxides are again given off.



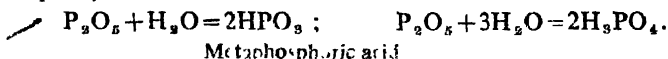
Sulphur trioxide and water react to produce sulphuric acid.



Phosphorus trioxide reacts with cold water forming phosphorus acid but with hot water it forms a gaseous substance named phosphine and phosphoric acid that remains in solution



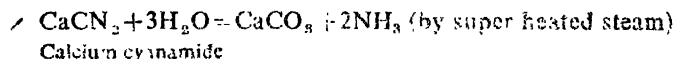
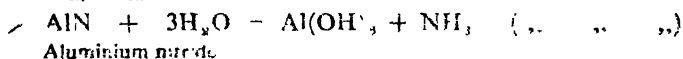
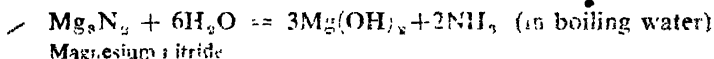
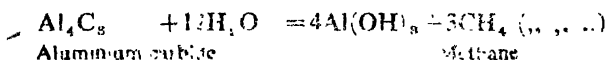
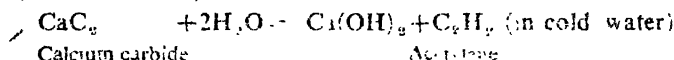
Phosphorus pentoxide reacts with cold water with a hissing sound producing meta phosphoric acid and with excess of water, it gives phosphoric acid.



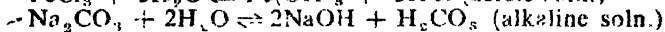
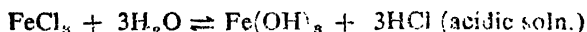
(8) Metallic hydrides (binary compounds of hydrogen and metals) react with water evolving hydrogen and forming the corresponding metallic hydroxides



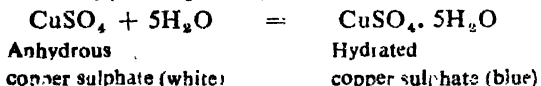
(9) Some metallic carbides (binary compounds of carbon and metals), some metallic nitrides (binary compounds of nitrogen and metals) and calcium cyanamide react with water



(10) Certain normal salts are hydrolysed by water giving either acidic or alkaline solutions.



Tests : (1) It is usually recognised by its capacity to turn anhydrous copper sulphate (white) to a blue colour.



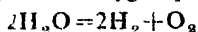
(2) At normal pressure, pure water freezes at 0°C and boils at 100°C. By determining the boiling point, it is also recognised.

(3) When a few drops of water are added to a lump of freshly burnt quick lime, the lime crumbles to powder with a hissing sound evolving much heat.

— **Composition of water :** The composition of water has been determined both volumetrically and gravimetrically.

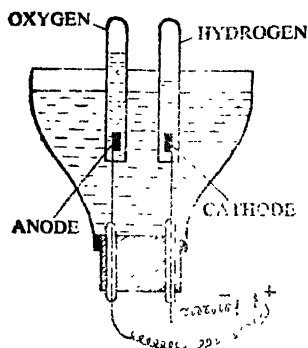
Volumetric composition of water : The composition of water by volume can be arrived at by both analytical and synthetic methods.

— **Analytical method :** In this method, the volumetric relation of hydrogen and oxygen in water is determined by measuring the volumes of hydrogen and oxygen produced on electrolysis of water.



A glass basin containing two very narrow glass tubes fused at its bottom is taken. After introducing two fine platinum wires through the tubes, the open ends of them are sealed. The upper ends of the wires are provided with two foils of the same metal. Now two-thirds of the basin are filled with water so that the two platinum foils remain completely immersed in the liquid.

A very little dil. sulphuric acid is added to increase the conductivity of water. Two graduated glass tubes filled entirely with the same acidulated water are inverted over the platinum foils. The ends of the platinum wires outside the basin are connected with the positive and negative poles of a battery and the current is switched on. Bubbles of gas appear near the foils and collect by displacement of the liquid in the tubes. After some time, platinum wires are disconnected and it is found that the volume of the gas collected in the graduated tube containing the anode is nearly half of the volume of the gas collected in the tube containing the cathode. A lighted taper when held at the gas collected over the cathode is extinguished but the gas continues to burn with a pale blue flame, so, the gas liberated over the cathode is hydrogen. That the gas collected at the anode is oxygen is proved by the fact that it rekindles a glowing chip of wood but itself does not burn. It produces brown fumes when brought in contact with nitric oxide.



(Fig. 2(1)) Electrolysis of water

From the above experiment, it is concluded that water is composed of two volumes of hydrogen and one volume of oxygen.)

Synthetic method : (Cavendish's modified method) Determination of the volumetric relation of hydrogen and oxygen in water by this method is based on the fact that water is formed when a mixture of two volumes of hydrogen and one volume of oxygen is ignited by means of an electric spark. $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$.

A straight eudiometer tube having two platinum wires sealed near the closed end for sparking is completely filled with pure and dry

mercury and inverted over a trough of the same liquid metal. A mixture of dry and pure hydrogen and oxygen in the ratio of 2 : 1 by volume is introduced into the eudiometer tube by displacement of

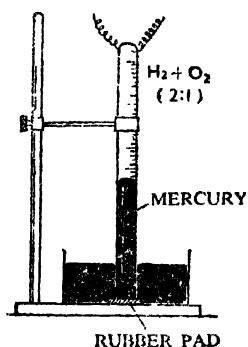


Fig. 2 (22) Volumetric composition of water by synthetic method

mercury. The open end of the tube is firmly pressed against a rubber pad within the trough. Usually the mixture of hydrogen and oxygen (electrolytic gas) obtained by electrolysis of acidulated water is dried by conc. sulphuric acid and is collected in the eudiometer tube. Now, an electric spark is passed through the mixture by connecting the platinum wires with an induction coil. The combination of hydrogen and oxygen takes place with explosion. On allowing the tube to cool, drops of water appear on the walls of the tube. The volume of water formed is negligible in comparison with the volumes of hydrogen and oxygen used up. On releasing the tube from the rubber pad, mercury from the trough rushes in and entirely fills the tube. It follows from the observation that no unreacted gas, either hydrogen or oxygen, is left in the tube.

Thus, the experiment proves that water is produced by the combination of two volumes of hydrogen and one volume of oxygen.

Volumetric composition of steam—Hofmann's method: The volumetric composition of steam is determined by this method by sparking 2 volumes of hydrogen with 1 volume of oxygen at a temperature higher than 100°C which is the condensation point of steam or boiling point of water.

The mixture of hydrogen and oxygen obtained by electrolysis of water acidified with a little dilute sulphuric acid is freed from moisture by passing it through conc. sulphuric acid. This dried mixture is used in this process.

The apparatus used in this process consists of a stout U-shaped eudiometer tube, one limb of which is closed and graduated. Near the closed end, two platinum wires are sealed into the glass for sending electric spark into the gas mixture. The other limb of the eudiometer tube is open and has a side cock near the bottom. This limb serves as a manometer, for mercury can be run into and out of this tube, so altering the pressure. The closed limb is surrounded by a jacket of a wider glass tube which is provided with two tubes, one at the top and the other at the bottom. The tube at the top serves as the inlet for introducing amyl alcohol vapour into the jacket while the tube at the bottom acts as an outlet of the same.

The closed and graduated limb is completely filled with mercury and a mixture of pure hydrogen and oxygen in the ratio of 2 : 1 by

volume is introduced into it by the displacement of mercury. Vapour of amyl alcohol (which boils at 132°C) is then passed continually through the wider tube serving as the jacket. When the mixed gas in the closed limb attains a steady temperature, the exact volume of the gas mixture is noted after equalizing the mercury levels in the two limbs. In order to reduce the pressure inside the closed limb, some mercury is taken out by means of the side cock. The open limb of the apparatus is then firmly plugged so that the mercury is not blown out. The gas mixture is then exploded by passing an electric spark into it from an induction coil through the platinum wires. Under the influence of the spark, hydrogen and oxygen combine to produce steam which cannot condense into water at this high temperature. The plug is removed. On allowing the gas to cool down to about 132°C , and bringing the mercury to the same level in both

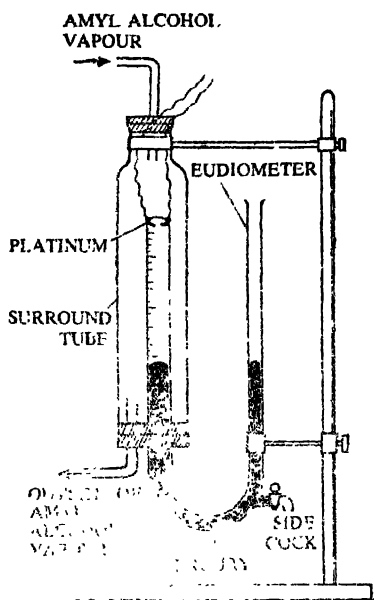


Fig. 2(23) Determination of volumetric relation of hydrogen and oxygen

the limbs, the volume is again noted. It is found that a contraction in volume has taken place and the volume of steam produced is exactly two-thirds of the volume of the mixture of hydrogen and oxygen originally introduced.

Passing of amyl alcohol vapour is then stopped and the whole apparatus is allowed to cool down gradually to the room temperature. Now, steam condenses to liquid water which occupies a negligible volume. Mercury level rises up slowly and finally the closed limb is seen to be filled up completely by mercury. This proves beyond doubt that all hydrogen and oxygen have been used up and the steam produced occupies two-thirds the volume.

Therefore, 2 volumes of hydrogen combine with 1 volume of oxygen to produce 2 volumes of steam, i.e. by volume,

Hydrogen : oxygen : steam = 2 : 1 : 2.

N.B. (1) Before each measurement of volume, the levels of mercury in the two limbs are to be adjusted to equality. Under this condition, the pressure of the gas or the gas mixture becomes equal to the atmospheric pressure at the temp. of the experiment.

Gravimetric composition of Water : There are two methods which are chiefly used in determining the composition of water by weight—(a) Dumas' method and (b) Morley's method.

Dumas' method—Principle : This method is based upon the fact that when perfectly pure and dry hydrogen is passed over previously weighed heated cupric oxide, hydrogen is oxidised to water and cupric oxide is reduced to metallic copper. $\text{CuO} + \text{H}_2 = \text{Cu} + \text{H}_2\text{O}$. Hence, from the weight of water formed and the loss in weight of cupric oxide, it is possible to find out the weights of hydrogen and oxygen used to form a definite amount of water.

Procedure : Hydrogen gas prepared in a Woulfe's bottle is purified and dried by allowing it to pass in succession through a series of 'U' tubes containing (a) lead nitrate solution, (b) silver sulphate solution, (c) strong caustic potash solution and (d) conc sulphuric acid. Finally, the gas is dried by passing it through a tube containing phosphorus pentoxide.

Now, the pure and dry hydrogen is passed through one end of a large bulb tube containing dry cupric oxide. The bulb tube with its content is previously weighed. The other end of the bulb tube is connected to a weighed U-tube containing fused calcium chloride. A P_2O_5 -guard tube is attached to the free end of the CaCl_2 U-tube to prevent the entry of moisture into the U-tube from the atmosphere (Guard tube has not been shown in the fig.) All connections must carefully be made air-tight. When the air from inside the whole apparatus has been completely replaced by hydrogen, the

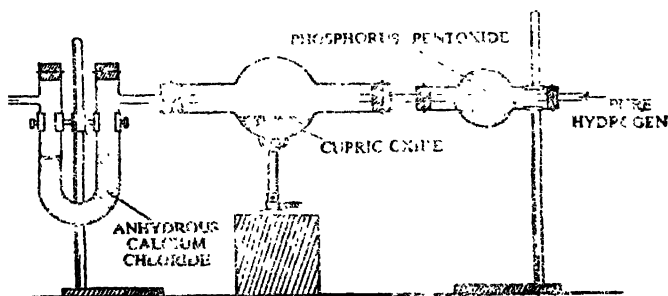


Fig. 2(24) Determination of gravimetric composition of water—Dumas' method

bulb tube is strongly heated. By taking oxygen from the oxide, hydrogen is oxidised to water which passes off in the form of vapour and is absorbed in the CaCl_2 U-tube. Cupric oxide is reduced to metallic copper which remains in the bulb-tube.

After the experiment, the apparatus is cooled to the laboratory temperature in a current of hydrogen. The bulb tube and the U-tube containing fused calcium chloride are detached and weighed separately with care. The increase in weight of U-tube gives the weight

of water formed and the loss in weight of bulb tube indicates the weight of oxygen which has been used up in forming water. On subtracting the weight of oxygen from the weight of water formed, the weight of hydrogen can be calculated.

Calculations : Let

wt of the bulb tube + cupric oxide before expt. = W_1 gms.

" " " " + copper + cupric oxide after expt. = W_2 gms

∴ wt of oxygen used up in producing water = $(W_1 - W_2)$ gms.

wt of U-tube containing CaCl_2 before expt. = W_3 gms.

" " " " after " = W_4 "

∴ wt of water produced = $(W_4 - W_3)$ gms

wt of hydrogen used up to produce $(W_4 - W_3)$ gms

of water = wt of water produced - wt of oxygen used up.

= $[(W_4 - W_3) - (W_1 - W_2)]$ gms.

∴ $[(W_4 - W_3) - (W_1 - W_2)]$ gms of hydrogen combine chemically with $(W_1 - W_2)$ gms of oxygen to produce $(W_4 - W_3)$ gms of water.

On performing the experiment carefully, it is found that the ratio of the weight of hydrogen to that of oxygen is 1 : 7.98.

So, it may be concluded that 1 part by wt. of hydrogen combines with 8 parts by wt. of oxygen to form 9 parts by wt. of water.

Precautions : (1) Hydrogen to be used in Dumas' method must be pure and free from moisture.

(2) All connections must be air-tight.

(3) Water vapour produced must completely be carried by the stream of hydrogen into the CaCl_2 -U-tube for absorption. The apparatus is allowed to cool in a current of hydrogen which prevents water from being carried backwards and re-oxidation of copper.

(4) There must be a CaCl_2 -guard tube attached to the end of the system with a view to preventing the entry of the moisture from the atmosphere.

(5) The bulb tube must be heated after the air has been completely expelled from inside the apparatus by hydrogen. This is necessary because hydrogen may combine with the oxygen in the bulb tube to form water.

Defects in Dumas' expt. : (1) Reduced copper in the glass tube (bulb) retains a minute amount of hydrogen when cooled in the current of the gas. This occluded hydrogen may slightly increase the weight of the glass tube.

(6) Hydrogen required in this experiment is purified by passing it through conc. sulphuric acid. A small amount of dissolved oxygen in the acid passes on with hydrogen and may oxidise copper to copper oxide affecting the weight of the tube. This oxygen may again be reduced to water.

However, the results of the experiment do not vary to any appreciable extent due to these defects which may be ignored.

Morley's experiment : This method of determination of accurate composition of water by weight is based on the synthesis of water from its elements. In this process, a known weight of hydrogen is burnt in a weighed quantity of pure oxygen to produce water by means of electric spark. $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$

The gravimetric composition of water is then determined from the weights of hydrogen and oxygen taken and the weight of water produced.

The apparatus used by Morley for his experiment is shown in fig. 2 (25). It consists of a specially constructed glass tube called reaction tube having two side tubes filled with phosphorus pentoxide and ending in jets inside the reaction tube.

Two pieces of platinum wires are fused near the jets. The upper ends of the side tubes serve as the inlets of the reacting gases ($H_2 + O_2$) separately and are provided with stop cocks. The reaction

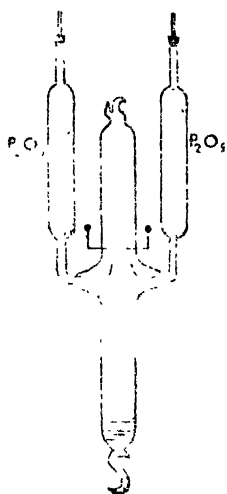


Fig. 2(25) Morley's experiment

or the central tube is so designed that the water formed may be collected at its lower part. The whole apparatus is evacuated and weighed accurately.

Now, the hydrogen produced by electrolysis of dil. sulphuric acid is purified by passing it successively through solid caustic potash, heated copper and phosphorus pentoxide. Pure hydrogen thus obtained is absorbed in palladium in an evacuated glass globe. The weight of the glass bulb containing palladium and occluded hydrogen is taken correctly. Oxygen prepared from potassium chlorate is purified by passing it through solid caustic potash, conc. sulphuric acid and phosphorus pentoxide in succession and is led into an evacuated bulb. This bulb along with oxygen is weighed. Now hydrogen and oxygen are led separately into side tubes containing phosphorus pentoxide. Immediately, an electric spark is passed between the platinum wires when the gases burn at the jets to produce steam. During burning, the reaction tube is dipped in cold water so that the steam produced is converted into liquid water and collects at the lower part of the tube. To facilitate complete conversion of steam into water, the apparatus is cooled in ice. By means of the stop-cocks, the entries of the gases are so regulated that hydrogen and oxygen in the ratio of 2 : 1 are introduced for combination. The unreacted gases are then pumped out through the P_2O_5 -tubes, analysed and their weights are found out. The loss of water during purifying is prevented by phosphorus pentoxide. The whole apparatus is next re-weighed accurately. The increase in weight of the apparatus gives the weight of water produced. The bulb in which hydrogen was absorbed in palladium and the bulb in which oxygen was kept before the experiment are weighed.

Calculations : Let

Wt. of the bulb containing hydrogen before expt = W_1 gms
 " " " " " " " " after " = W_2 "

$$\begin{aligned}
 \therefore \text{Wt. of hydrogen introduced} &= (W_1 - W_2) \text{ gms.} \\
 \therefore \quad \quad \quad \text{left} &= W_3 \text{ gms.} \\
 \therefore \quad \quad \quad \text{burnt} &= (W_1 - W_2) - W_3 \text{ gms.}
 \end{aligned}$$

Wt. of the bulb containing oxygen before exp^t = W_4 gms.

$$\begin{aligned}
 \therefore \text{Wt. of oxygen introduced} &= W_5 \text{ gms.} \\
 \therefore \quad \quad \quad \text{left} &= (W_4 - W_5) \text{ gms.} \\
 \therefore \quad \quad \quad \text{used up in combination} &= (W_4 - W_5) - W_6 \text{ gms.}
 \end{aligned}$$

Let the wt. of water produced be W gms.

From the results of a number of experiments, Morley obtained the ratios,

$$O : H = (W_4 - W_5) - W_6 : (W_1 - W_2) - W_3 = 7.9395 : 1$$

$$\text{and } H_2O : H = W : (W_1 - W_2) - W_3 = 8.9395 : 1$$

\therefore 8 parts by weight of oxygen combine with 1 part by weight of hydrogen to form 9 parts by weight of water.

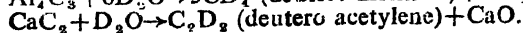
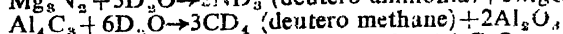
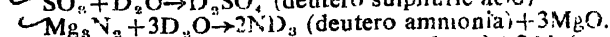
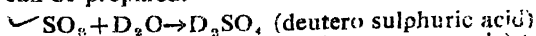
(✓) **Heavy water or Deuterium oxide* D_2O** : Heavy water is an oxide of heavy hydrogen or deuterium, an isotope of ordinary hydrogen. (the atomic masses of ordinary hydrogen and deuterium are approximately 1 and 2 respectively).

It is best prepared by electrolysis of the residual water accumulated in the electrolytic cells used for several years for industrial production of hydrogen.

Heavy water resembles ordinary water in composition but is likely to possess properties different from those of ordinary water as it contains two heavier hydrogen atoms in its molecule. Both the ordinary water and heavy water are colourless liquids. Heavy water differs from ordinary water in many physical properties as shown in the following table.

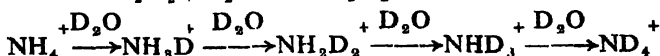
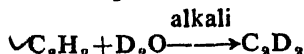
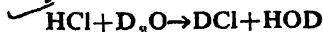
Property	Ordinary water (H_2O)	Heavy water (D_2O)
Sp. gravity at 20°C	0.9982	1.1059
Freezing point	0°C	3.82°C
Boiling point	100°C	101.4°C
Tempr. of maximum density	4°C	11°C
Dielectric constant at 20°C	82	80.5

Heavy water is poorer electrolytic solvent than ordinary water. Starting from heavy water, a number of deuterium compounds can be prepared.



* Not included in the W.B.H.S. Syllabus.

The hydrogen atoms of many hydrogen compounds are exchanged by deuterium when treated with D_2O .



Uses : (1) Heavy water is used as a source of heavy hydrogen
(2) It is used in the study of mechanism of chemical reactions and elucidating the constitutions of some organic compounds. (3) In recent years, it finds its important applications in nuclear chemistry.

HYDROGEN PEROXIDE

Mol. formula H_2O_2
Sp. gr. at $0^\circ C$ 1.46

Mol. wt. 32.016
Boiling point $151^\circ C$

In 1819, Thenard discovered the compound and named it oxygenated water.

Preparation : (1) By the action of dil. mineral acids on certain metallic peroxides

(A) **Laboratory method of preparation :** In the laboratory, hydrogen peroxide is prepared by the interaction of cold, dil sulphuric acid and hydrated barium peroxide. Insoluble barium sulphate is produced at the same time.



Finely powdered barium peroxide taken in a beaker is made into a thin paste of hydrated barium peroxide ($BaO_2 \cdot 8H_2O$) by slowly stirring with a small quantity of water. Dil sulphuric acid is taken in another beaker. Both the beakers are cooled by placing them in a freezing mixture of ice and salt. When the temperature falls to about $0^\circ C$, the paste is added gradually to ice-cold dilute acid and the mixture is slowly but constantly stirred with a glass rod.

Barium peroxide reacts with the acid to form hydrogen peroxide which remains in solution and a white precipitate of barium sulphate. Addition of the paste is continued until the solution is just faintly acidic. Slight acidity increases the stability of hydrogen peroxide. The precipitated barium sulphate is allowed to settle and is filtered off. The filtrate thus obtained is a solution of hydrogen peroxide in water containing 10-20% H_2O_2 .

(B) In place of dil. sulphuric acid, phosphoric acid may be used for preparing hydrogen peroxide. In this case, hydrogen peroxide along with insoluble barium phosphate is produced. The presence of a small quantity of phosphoric acid in hydrogen peroxide retards its

decomposition. Here, phosphoric acid behaves as a negative catalyst. On filtering the precipitated barium phosphate, an aqueous solution of hydrogen peroxide is obtained.

N.B. (1) In the preparation of hydrogen peroxide, cold and dilute sulphuric acid is used. Hydrogen peroxide tends to decompose spontaneously into oxygen and water even at the ordinary temperature. This decomposition is considerably accelerated by heat. Hydrogen peroxide decomposes more readily at the temperature produced by the action of conc. sulphuric acid on barium peroxide.

(2) Anhydrous barium peroxide is not used in this preparation for two reasons :

(i) The heat generated by the interaction of anhydrous barium peroxide and the acid affects the stability of hydrogen peroxide. (ii) Moreover, particles of anhydrous barium peroxide are soon coated with a layer of insoluble barium sulphate. This coating prevents the metallic peroxide from coming in contact with the acid and the action consequently ceases.

(3) The thin paste of barium peroxide is added to the cold and dilute acid in such a way that it mixes uniformly throughout,

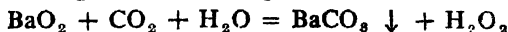
(4) The decomposition of hydrogen peroxide is slowed down by the presence of a trace of the acid which acts as negative catalyst. If excess of barium peroxide is added, hydrogen peroxide formed begins to decompose. This is why the solution is kept slightly acidic at the end of the reaction.

(5) Hydrochloric acid is not suitably used. Soluble barium chloride which is produced by the action of barium peroxide and hydrochloric acid cannot be removed easily from the aqueous hydrogen peroxide solution.

(c) Hydrogen peroxide may also be prepared by the action of carbonic acid on barium peroxide. This process of preparation is known as Merck's process.

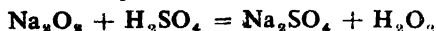
Merck's process :

Finely powdered barium peroxide is suspended in water in a beaker cooled in crushed ice. A stream of carbon dioxide is then passed through the cooled mixture until the water becomes just acidic. Hydrogen peroxide and insoluble barium carbonate are formed according to the following reaction.



The precipitated barium carbonate is filtered off when a solution of hydrogen peroxide in water is obtained.

Merck's perhydrol : A 30% solution of hydrogen peroxide which is sold under the trade name Merck's perhydrol is obtained by the interaction of sodium peroxide and dilute sulphuric acid.



Calculated amount of sodium peroxide is slowly added to dilute (20%) sulphuric acid cooled in a freezing mixture of ice and salt. Sodium sulphate formed separates at this low temperature as crystalline Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and is filtered off. The filtrate on distillation under reduced pressure yields 30% solution of hydrogen peroxide or perhydrol.

(d) Hydrogen peroxide is also obtained by adding calculated quantity of sodium peroxide to an ice-cold solution of mono sodium dihydrogen phosphate (NaH_2PO_4) until the solution only just reacts acid. $\text{Na}_2\text{O}_2 + 2\text{NaH}_2\text{PO}_4 = 2\text{Na}_2\text{HPO}_4 + \text{H}_2\text{O}_2$

On further cooling, disodium hydrogen phosphate separates out as $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ which is removed by filtration. The filtrate is a strong solution of hydrogen peroxide in water.

Preparation of pure hydrogen peroxide : Hydrogen peroxide resulting from the reaction of a peroxide and dilute acid is obtained only in aqueous solution. Water and hydrogen peroxide cannot be separated from each other by fractional distillation as hydrogen peroxide decomposes into oxygen and water at a temperature far below its boiling point. Hence, the dilute aqueous solution of hydrogen peroxide is concentrated by distilling under reduced pressure at relatively low temperature. Water is more volatile than hydrogen peroxide (b. p. of water 100°C and that of hydrogen peroxide 151°C).

An initial concentration is made by evaporating the aqueous solution slowly in an open glass or porcelain basin on water-bath at $60\text{--}70^\circ\text{C}$ until effervescence begins. At this stage, more volatile water vaporises and concentration of hydrogen peroxide remaining behind reaches to about 66 percent. Further concentration by this process results in the rapid decomposition of hydrogen peroxide.

The solution containing 66% hydrogen peroxide is then subjected to distillation under reduced pressure of 15 m.m. at 85°C whereby about 99% pure hydrogen peroxide is obtained. The remaining portion of water is removed by drying the liquid over conc. sulphuric acid in a vacuum desiccator. Crystals of pure hydrogen peroxide separate if 99% solution hydrogen peroxide is cooled to -10°C followed by seeding with a crystal of hydrogen peroxide previously obtained by cooling a portion of 99% solution in solid carbon dioxide and ether.

✓ **Description of the process of concentration of hydrogen peroxide solution under reduced pressure :**

The aqueous solution of hydrogen peroxide (66 percent) is taken in a round-bottom distilling flask fitted with a thermometer and placed on a water bath [Fig 2(26)]. The side tube of the flask is connected with a Liebig's condenser the end of which is introduced into another distilling flask acting as a receiver. All connections must be air-tight. The side tube of the receiver is then connected with a manometer by a rubber tube and is attached to a water pump through an empty filtering flask. The liquid inside the distilling flask is heated on the water bath slowly to about $30\text{--}35^\circ\text{C}$ under a pressure of 15 m.m. and the water tap is kept open when mainly water distills over and collects in the receiver. The receiver is then changed and the distillation is continued at $70\text{--}80^\circ\text{C}$. Repeated distillation under reduced pressure yields hydrogen peroxide of 99 percent purity. As usual, the remaining portion of water is removed by keeping the 99% solution over conc. sulphuric acid in a vacuum desiccator.

By electrolytic process: Hydrogen peroxide is nowadays prepared by electrolysis of 50% sulphuric acid at low temperature with copper cathode and platinum anode. This is the modern process for a large scale preparation of the compound.

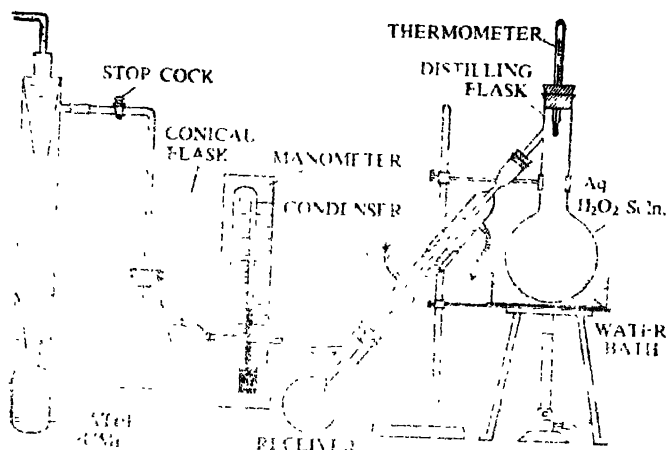
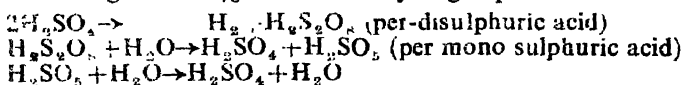


Fig. 2(26) Purification of hydrogen peroxide

As a result of electrolysis, perdisulphuric acid ($\text{H}_2\text{S}_2\text{O}_8$) is first formed at the anode due to anodic oxidation. The resulting per disulphuric acid is then hydrolysed by water to produce hydrogen peroxide. The dilute solution on distillation under reduced pressure at $80-90^\circ\text{C}$ gives a 30% solution of hydrogen peroxide.



In another process, hydrogen peroxide is prepared by electrolyzing a solution of ammonium bisulphate at low temperature.

Properties—Physical: (1) Hydrogen peroxide is a colourless, transparent, syrupy liquid. In thick layers, it is bluish in colour. It has an irritating odour resembling that of nitric acid.

(2) It is soluble in water in all proportions and also highly soluble in organic solvents like alcohol, ether etc. When 99% solution of hydrogen peroxide is cooled by solid or liquid carbon dioxide and ether, crystals of pure hydrogen peroxide ($\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$) separate out.

(3) Its specific gravity is 1.46 at 0°C . It solidifies at -1.7°C and boils at 151°C . (It boils at 84°C under a pressure of 68 mm.)

(4) In a concentrated form, hydrogen peroxide produces a white blister on skin.

- ✓ **Chemical :** (1) *Hydrogen peroxide is not a stable compound* At ordinary temperature, it decomposes slowly into water and oxygen liberating considerable amount of heat



This decomposition is accelerated by heat, by light or in contact with a rough surface. Finely divided metals like gold and platinum, manganese dioxide, iodine or alkalis present in ground glass act as catalysts and cause rapid decomposition of hydrogen peroxide.

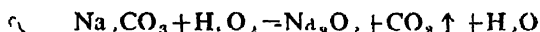
To avoid explosion, due to the accumulation of active oxygen, it is advised to cool a bottle of hydrogen peroxide before opening,

Hydrogen peroxide when heated to its boiling point (151°C) decomposes into oxygen and steam with explosive violence

Small quantities of sulphuric acid, phosphoric acid, calcium chloride, glycerine etc. retard the decomposition of hydrogen peroxide as inhibitors and are often added to the commercial products as preservatives

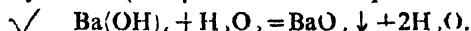
The decomposition is minimised if hydrogen peroxide is stored in a bottle made of polythene.

(2) *It is feebly acidic :* A dilute solution of hydrogen peroxide is neutral and has no effect on an indicator. When pure, hydrogen peroxide turns blue litmus red and reacts with some alkalis. It reacts with a solution of sodium carbonate to produce sodium peroxide and carbon dioxide.

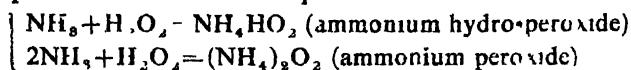


If excess of carbonate is used hydrogen peroxide is catalytically decomposed to evolve oxygen

With a solution of barium hydroxide, hydrogen peroxide gives a white crystalline precipitate of barium peroxide



In the pure state, it reacts also with ammonia to give ammonium hydroperoxide and ammonium peroxide.

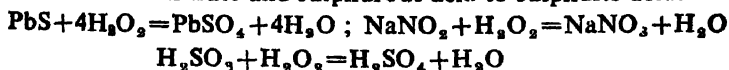


In the above reactions, hydrogen peroxide exhibits its acid properties. Peroxides produced are the true salts of hydrogen peroxide.

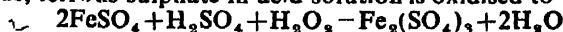
(3) *Hydrogen peroxide is a powerful oxidising agent* Hydrogen peroxide contains in its molecule one loosely bound oxygen atom which is easily detached in the atomic state. $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}$

The oxidising action is usually explained by the readiness with which hydrogen peroxide in aqueous solution gives rise to atomic oxygen. It sets fire to a mixture of magnesium powder and manganese dioxide or powdered carbon and manganese dioxide. It inflames cotton and wood.

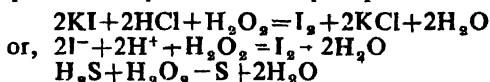
It oxidises black lead sulphide to white lead sulphate, sodium nitrite to sodium nitrate and sulphurous acid to sulphuric acid.



Hydrogen peroxide oxidises acidified ferrous salts to ferric salts. Thus, ferrous sulphate in acid solution is oxidised to ferric sulphate.



Acidified potassium iodide solution is quantitatively oxidised by hydrogen peroxide to iodine. A brown colouration appears due to the liberation of free iodine. Hydrogen peroxide oxidises hydrogen sulphide to sulphur which is precipitated.

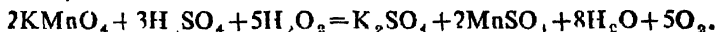


In all the above oxidation reactions, hydrogen peroxide is reduced to water.

It bleaches delicate materials like silk, wool, feather etc. by oxidation. It bleaches black hair to golden yellow colour.

(4) *In certain reactions, hydrogen peroxide appears to behave as a reducing agent*

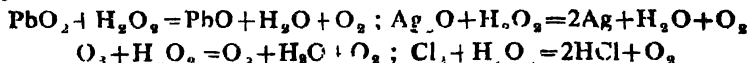
On addition of hydrogen peroxide to a potassium permanganate solution acidified with dilute sulphuric acid the latter is rapidly reduced to manganous salt. The pink coloured solution becomes colourless and oxygen evolves as one of the products. Here, KMnO_4 is changed into MnSO_4 i.e. the heptavalent manganese (Mn^{+7}) has been converted to bivalent manganese (Mn^{+2}). So, it is an example of reduction.



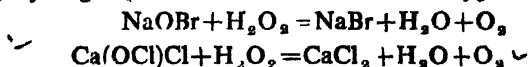
Potassium dichromate (orange in colour) in acid solution is reduced to a green solution due to the formation of chromic salt. In this reduction, hexavalent chromium (Cr^{+6}) is reduced to its trivalent state (Cr^{+3}).



Hydrogen peroxide reduces lead dioxide into lead monoxide, silver oxide into metallic silver, ozone to oxygen, chlorine to hydrochloric acid.



Sodium hypobromite and bleaching powder solutions are reduced by hydrogen peroxide with evolution of oxygen.



It is to be noted that only strong oxidising agents such as KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ etc are reduced by hydrogen peroxide and

in all the above reactions, gaseous oxygen is evolved as one of the products.

Here, hydrogen peroxide which apparently acts as a reducing agent is not oxidised. It actually loses one atom of oxygen and is reduced to water. The liberated oxygen combines with an atom of oxygen from another reactant to form a molecule of oxygen.

However, in the light of change of oxidation number, hydrogen peroxide can be shown to behave as an oxidising agent as well as a reducing agent. The oxidation numbers of oxygen in hydrogen peroxide, water and elementary state are -1 , -2 and 0 (zero) respectively. Thus when H_2O_2 is converted to H_2O , the oxidation number of oxygen decreases from -1 to -2 . So, it can act as an oxidising agent; when the peroxide is converted to oxygen, the oxidation number of oxygen increases (from $-1 \rightarrow 0$) indicating its behavior as a reducing agent.

(5) *Hydrogen peroxide is capable of forming addition compounds*: It forms addition products with some salts. Thus, with potassium fluoride and ammonium sulphate, it gives $KF \cdot H_2O_2$ and $(NH_4)_2SO_4 \cdot H_2O_2$. With urea, the crystalline addition compound $[CO(NH_2)_2 \cdot H_2O_2]$ known as hyperol is obtained. In these compounds, hydrogen peroxide behaves like water of crystallisation.

Experiments to illustrate the important properties of hydrogen peroxide :

(1) *It is an unstable compound* and decomposes easily to give oxygen. A little hydrogen peroxide is taken in a test tube and a pinch of manganese dioxide is added to it. A rapid evolution of a colourless gas takes place. A glowing chip of wood is immediately rekindled in the gas and the gas is absorbed by alkaline potassium pyrogallate solution. These prove that the gas evolved is oxygen and manganese dioxide catalyses the decomposition of hydrogen peroxide.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

(2) *Hydrogen peroxide possesses strong oxidising properties*:
(a) A piece of lead acetate paper is blackened by hydrogen sulphide due to the formation of lead sulphide (black). When this piece of paper is treated with a solution of hydrogen peroxide, the black colour disappears. This change of colour is due to the fact that hydrogen peroxide oxidises black lead sulphide to white lead sulphate.

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O$$

The colour of the old oil-paintings which have been blackened due to long exposure to air is restored by washing with hydrogen peroxide. The white lead pigment of the paint is gradually converted into black lead sulphide by the action of hydrogen sulphide present in the atmosphere. Hydrogen peroxide removes the black colour by oxidation.

(b) A solution of potassium iodide is taken in a test tube and acidified with dil. hydrochloric acid. On adding hydrogen peroxide to the acidified iodide solution, iodine is set free and the solution appears brown. This liberated iodine turns starch paper blue,

Tests : (1) Hydrogen peroxide turns acidified starch-potassium iodide paper blue. (Here, hydrogen peroxide liberates iodine from KI in acid solution and the liberated iodine forms a blue compound with starch). (2) A piece of paper soaked in lead acetate solution is

blackened by hydrogen sulphide. This black paper when treated with hydrogen peroxide solution turns white. (3) When a solution of potassium dichromate acidified with dilute sulphuric acid is added to hydrogen peroxide and shaken with ether, the ethereal layer becomes deep blue in colour. (4) It readily decolourises the pink colour of potassium permanganate solution acidified with dil. sulphuric acid (5) Hydrogen peroxide when added to a solution of titanium dioxide in dilute sulphuric acid, an orange yellow colour develops.

Strength of hydrogen peroxide solution : It is customary to state the strength of hydrogen peroxide solution in terms of volume and it is sold as of 10 vol, 20 vol, 30 vol etc. strength.

The strength in volume actually means the volume in cc. of oxygen evolved at N.T.P. when a unit volume hydrogen peroxide solution is decomposed by heat or by contact with a catalyst. Thus, 20 volume hydrogen peroxide signifies that a given volume of this solution will give 20 times its volume of oxygen at N.T.P. when decomposed or 1 cc. of hydrogen peroxide of 20 volume strength on heating will produce 20cc. of oxygen under normal conditions of temperature and pressure ; Obviously at N.T.P., if volume of a sample of hydrogen peroxide solution liberates x times its volume of oxygen, the strength of the solution is x V.

We know, $2\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}_2$
 $\frac{68}{22400 \text{ c.c. at N.T.P.}}$ (According to Avogadro's hypothesis)

\therefore At N.T.P. 68 gms of hydrogen peroxide liberate 22400 cc. of oxygen

\therefore 1 gm " " " " liberates $\frac{22400}{68}$ or 329.4 cc. of oxygen

i.e. 100 cc. of 1% solution of hydrogen peroxide liberate 329.4 cc. of oxygen.

or, 1 cc. of 1% solution of hydrogen peroxide liberate 3.294 cc. or oxygen

\therefore 1% solution of hydrogen peroxide is of 3.294 volume strength

Hence, 1 volume of hydrogen peroxide is of $\frac{1}{3.294}$ per cent strength

or, 10 volume " " " " of $\frac{10}{3.294}$ " "

\therefore A sample of hydrogen peroxide of V volume strength is of $\frac{V}{3.294}$ per cent strength.

Now, equivalent weight of $\text{H}_2\text{O}_2 = \frac{34}{2} = 17$.

A (N) H_2O_2 solution contains 17 gms of H_2O_2 per litre.

\therefore 1cc. of (N) H_2O_2 solution contains 0.017 gm of H_2O_2

Now, 68 gms of H_2O_2 on decomposition yield 22400 c.c. of oxygen at N.T.P.

\therefore 0.017 gm of H_2O_2 on decomposition yields $\frac{22400 \times 0.017}{68}$ or

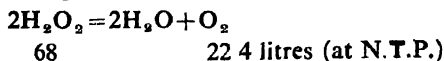
5.6 c.c. of oxygen of N.T.P.

\therefore 1 (N) H_2O_2 solution is of 5.6 volume strength.

Some problems on the strength of H_2O_2 :

(1) Find out the strength in gms per litre and also the percentage strength of a "5 volume" hydrogen peroxide solution.

According to the reaction



\therefore 68 gms of $\text{H}_2\text{O}_2 \equiv 22.4$ litres Oxygen (at N.T.P.)

Now according to the definition,

5 ml O_2 are obtained from 1 ml of 5 volume H_2O_2

\therefore 22.4 litres of O_2 ,, ,, 4.48 litres ,, ,,

\therefore 1 litre of 5 volume H_2O_2 contains $\frac{68}{4.48}$ or

15.2 gms H_2O_2 (approx)

Again, 1000 ml contains 15.2 gms of H_2O_2

\therefore 100 ,, ,, 1.52 ,, ,, ,,

5 volume H_2O_2 solution corresponds to 1.52% solution by weight.

(2) Calculate the volume strength of 3.4% solution of H_2O_2 .

According to the question,

100 ml of 3.4% solution contains 3.4 gms of H_2O_2

\therefore 1 ,, ,, ,, ,, 0.034 gm ,, ,,

Again, $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

68 22.4 litres (at N.T.P.)

\therefore Vol. of oxygen to be produced at N.T.P. from 0.034 gm of H_2O_2

$$= \frac{22400 \times 0.034}{68} \text{ ml} = 11.2 \text{ ml.}$$

\therefore 1 ml of H_2O_2 solution gives 11.2 ml of O_2 at N.T.P.

Hence, the volume strength of H_2O_2 solution is "11.2 volumes".

OZONE

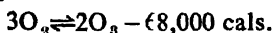
Mol. formula O_3

Mol. wt. 48

Density 24 (H=1)

In 1840, Schonbein proved the existence of a new gas by passing an electric discharge through air. He gave the name ozone (from the Greek, *Ozo.* to smell) to the new gas due to its peculiar fishy smell.

Preparation : Laboratory method : Usually ozonised oxygen i.e. ozone admixed with oxygen is best prepared by the passage of silent electric discharge through pure and dry oxygen (or air). Oxygen is partially converted into ozone.



This conversion is strongly endothermic. Two types of apparatus commonly used in the laboratory for the preparation of ozone are (a) Siemen's ozoniser and (b) Brodie's ozoniser.

Preparation of ozone in Siemen's Ozoniser :

Siemen's ozoniser or apparatus consists of two coaxial glass tubes fused with each other at one end. The outside of the outer tube and the inside of the inner one are coated with tin foils. The outer wider tube has two side tubes, one of which is meant for

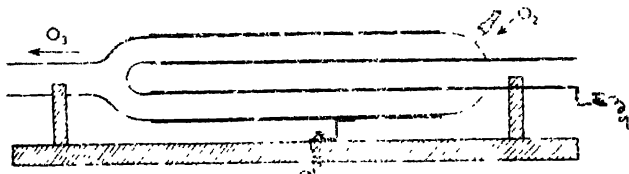


Fig. 2(27) Siemen's ozoniser

entry of oxygen and the other serves as an outlet for ozonized oxygen. The tin foils are now connected with the two terminals of an induction coil and a slow stream of pure and dry oxygen is passed through the annular space between the concentric tubes. Under the influence of silent electric discharge which passes between the tin foils separated by glass of the tubes, oxygen is partially converted into ozone and the gas coming out of the apparatus is a mixture of ozone and oxygen. This mixture under ordinary condition contains 7-10% of ozone. If air is used instead of oxygen, the conversion is about 1%.

Preparation of ozone in Brodie's Ozoniser :

Two concentric glass tubes constitute the main part of Brodie's ozoniser or apparatus. A narrow glass tube closed at the bottom is introduced into the wider limb of a U-shaped glass tube and the two are fused at the open ends. Thus, an annular space is left between the outer and the inner tubes. The inner tube is filled with dilute sulphuric acid into which is dipped a piece of platinum wire.

The outer tube i.e. the wide-limb of the U-tube is provided with a side tube through which oxygen enters into the apparatus. Comparatively narrow limb of the U-tube serves as an outlet for escape of ozonised oxygen. The whole apparatus is then kept immersed in a glass jar containing dil. sulphuric acid. A piece of platinum wire is also dipped into this acid solution.

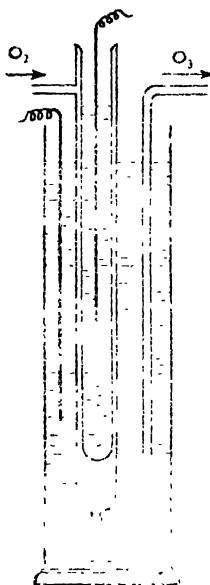


Fig 2(28) Brodie's ozoniser

Two platinum wires are now connected with the terminals of an induction coil and a slow current of pure and dry oxygen (or air) is passed through the side tube. The oxygen in the annular space between the two concentric tubes is thus subjected to a silent electric discharge and is partially converted into ozone. The issuing gas contains about 20% of ozone.

Preparation of pure ozone : Ozonised oxygen, when cooled in liquid air, condenses to a deep blue liquid which is a solution of ozone in liquid oxygen. This blue liquid is subjected to fractional distillation. Liquid oxygen evaporates first and is removed with the help of a pump. Less volatile liquid ozone is left behind. On careful vaporization of the liquid ozone, deep blue pure gaseous ozone is obtained. Ozone thus prepared soon begins to decompose. This process of purification must be done with extreme care as the liquid ozone is a highly explosive substance.

N.B. (1) The conversion of oxygen into ozone is a reversible, highly endothermic reaction. So, according to Le Chatelier's principle, the yield of ozone should increase with rising temperature. But in practice, ozone is never prepared by subjecting oxygen to a high temperature. Ozone tends to decompose into oxygen even at ordinary temperature; the decomposition will proceed rapidly at high temperatures. With a view to preventing its decomposition, ozone must be quickly cooled after its formation at high temperature.

(2) Ozone is prepared by passing silent electric discharge through oxygen. In the case of an ordinary electric discharge, much heat is generated. So, this is not permissible as the heat produced will decompose most of the ozone as soon as it is formed. By inserting an insulating material such as glass in the space between the electrodes through which the discharge passes, we get silent electric discharge producing much less heat. As a result, the decomposition of ozone is minimised.

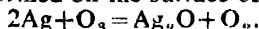
Properties—Physical : (1) Ozone is a deep blue gas with a disgusting fishy smell. (2) It can be condensed to a dark blue liquid. Liquid ozone (b.p. -112°C) is an explosive and magnetic substance. (3) It is slightly soluble in water but more soluble than oxygen. It dissolves in organic solvents like acetic acid, carbon tetrachloride etc. giving a deep blue solution. It is readily absorbed by oil of turpentine. (4) It is heavier than air or oxygen.

Chemical: (1) *Ozone is not a very stable compound.* Ozone tends to decompose into oxygen spontaneously at the ordinary temperature ;

but the rate of decomposition is slow. The decomposition is rapid at a higher temperature. (200°C) and in contact with dust particles, organic substances, finely divided platinum black, silver oxide, manganese dioxide, lead oxide, iron oxide, powdered glass etc. At 300°C, ozone is completely converted into oxygen. $2O_3 \rightleftharpoons 3O_2$

(2) *Ozone is much more active than oxygen and is a powerful oxidising agent.* It supports combustion of many substances. Its vigorous oxidising action is due to the nascent oxygen which readily comes out of its molecule. $O_3 \rightarrow O_2 + O$

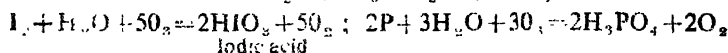
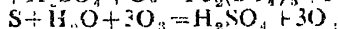
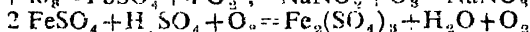
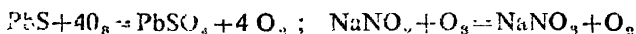
Most metals excepting gold and platinum are oxidised to their oxides by ozone. When ozone acts on warm metallic silver, a brown layer of oxide is formed on the surface of the metal.



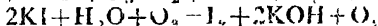
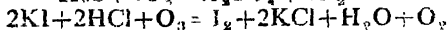
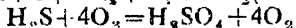
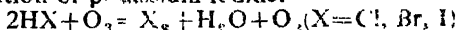
Mercury loses its mobility and metallic lustre in contact with ozone at the ordinary temperature. Ozone also causes mercury to adhere to the surface of the glass. This is presumably due to partial oxidation of mercury to mercurous oxide. $2Hg + O_3 = Hg_2O + O_2$

Ozone destroys the elasticity of rubber.

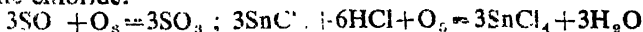
Ozone oxidises lead sulphide (black) to lead sulphate (white), sodium nitrite to sodium nitrate, acidified ferrous sulphate to ferric sulphate. Moist sulphur, phosphorus and iodine are oxidised to their higher oxyacids by ozone while moist ammonia is converted into ammonium nitrite and ammonium nitrate.



Ozone also oxidises hydrochloric acid (or hydrobromic or hydroiodic acid) to chlorine (or bromine or iodine) and hydrogen sulphide to sulphuric acid. It liberates iodine from acidified or neutral solution of potassium iodide.



In all the above oxidation reactions, ozone itself is reduced to oxygen. In a few reactions, the ozone molecule as a whole takes part in oxidation. Thus, ozone oxidises sulphur dioxide to sulphur trioxide and stannous chloride (acidified with hydrochloric acid) to stannic chloride.

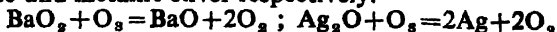


No evolution of oxygen occurs in the above oxidation processes.

(3) In certain cases, ozone appears to act as a reducing agent. Ozone reduces hydrogen peroxide to water withdrawing one atom of oxygen from the peroxide.



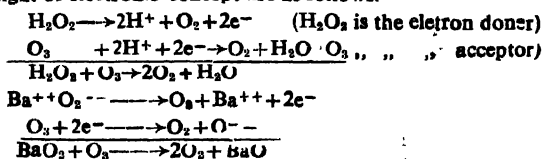
Similarly, barium peroxide and silver oxide are reduced by ozone to barium oxide and metallic silver respectively.



However, ozone has no action on potassium permanganate or dichromate.

In the true sense, ozone should not be regarded as a reducing agent. Ozone while exhibiting its so called reducing properties is not oxidised but reduced to oxygen.

According to the electronic theory of oxidation-reduction ozone, here acts as an electron acceptor and hence is an oxidising agent. These redox reactions in the light of electronic concept are as follows.



(4) It possesses bleaching properties. Ozone bleaches vegetable colours by oxidation. Indigo is bleached colourless in contact with ozone.

(5) *Power of forming addition compounds is a remarkable property of ozone* When ozone reacts with an unsaturated organic compound, an addition product known as ozonide is formed. Ethylene, benzene etc. thus form their respective ozonides.



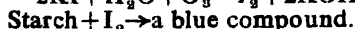
These ozonides when treated with water undergo hydrolysis giving hydrogen peroxide in most of the cases and other products which help in determining the constitution of the unsaturated compounds.

Uses : (1) Due to its disinfecting action, it is used in sterilization of water. It is also used in purification of air especially in underground railways, crowded halls, hospital chambers, animal houses.

(2) In the chemical laboratories, it is used in oxidising and elucidating the constitutions of organic compounds.

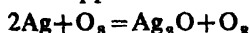
(3) It also finds its application as a bleaching agent for oils, waxes, flour etc.

Tests : (1) Ozone can be recognised from its strong fishy smell. (2) *Paper wetted with potassium iodide and starch solution is coloured blue in contact with ozone. Ozone liberates iodine from potassium iodide and the liberated iodine reacts with starch producing a blue colour. $2\text{KI} + \text{H}_2\text{O} + \text{O}_3 = \text{I}_2 + 2\text{KOH} + \text{O}_2$



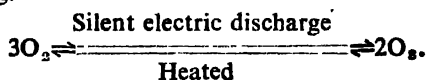
(3) Paper soaked in alcoholic benzidine solution is turned brown by ozone. (4) A little mercury is taken in a flask containing ozonised oxygen and shaken ; mercury loses its mobility and sticks to the glass. Moreover, the metal becomes dull in appearance. However,

on being shaken with water, mercury regains its fluidity and shining appearance. (5) When ozone and silver interact, a brown layer of silver oxide is formed on the surface of the metal. This reaction is sometimes applied in identification of ozone.



*This test is not specific for detection of ozone as H_2O_2 , Cl_2 , NO_2 etc. also respond to this test.

Oxygen and ozone are the allotropes of the same element : This is proved by the fact that each can be converted into the other without change of mass. Oxygen, when subjected to silent electric discharge, is changed to ozone, which, on the other hand, decomposes into oxygen on heating.



Pure and dry oxygen taken in a suitable apparatus is exposed to the action of silent electric discharge. Then, a piece of paper soaked in starch potassium iodide solution is held in the evolved gas. The paper turns blue indicating that the oxygen has been converted into ozone. This gaseous ozone on being heated to 300°C is completely decomposed into oxygen. A piece of starch potassium iodide paper is not coloured blue by the gas. This gas is absorbed by alkaline potassium pyrogallate solution and the resulting solution becomes brown in colour. This serves as a distinctive test for oxygen. Thus, it can be inferred that oxygen and ozone are the allotropes of the same element. The difference between them is one of molecular complexity, oxygen having a diatomic molecule O_2 and ozone a triatomic molecule, O_3 .

Comparison of the properties of oxygen and ozone :

Oxygen	Ozone
Colourless, odourless gas.	Pale blue gas with fishy odour.
Density 16(H=1)	Density 24 (H=1)
Insoluble in oil of turpentine.	Absorbed by turpentine.
Heat has no action.	Heat converts ozone into oxygen $2\text{O}_3 \rightarrow 3\text{O}_2$
No effect on mercury at room temperature.	Mercury in contact with ozone loses its mobility and wets glass.
No effect on rubber	Attacks rubber
Has no effect on potassium iodide solution.	Liberates iodine from potassium iodide solution. $\text{O}_3 + 2\text{KI} + \text{H}_2\text{O} = \text{O}_2 + 2\text{KOH} + \text{I}_2$
Cannot oxidise black lead sulphide.	Ozone oxidises black lead sulphide to white lead sulphate. $\text{PbS} + 4\text{O}_3 = \text{PbSO}_4 + 4\text{O}_2$

Comparison of the properties of ozone and hydrogen peroxide :

Property	Ozone	Hydrogen peroxide.
Physical properties	Blue gas with a fishy smell. It is the allotropic modification of oxygen.	Pale blue syrupy liquid having an odour resembling that of nitric acid. It is a peroxide.
Solubility	Slightly soluble in water, highly soluble in terpentine oil, carbon tetra chloride.	Readily soluble in water and organic solvents like ether, acetic acid etc.
Stability	Not very stable, slowly decomposes evolving oxygen at ordinary temp. Decomposition is accelerated by heat, by contact with rough surfaces, dust particles, manganese dioxide, platinum black etc. $2\text{O}_3 \rightleftharpoons 3\text{O}_2$	Hydrogen peroxide has the tendency to decompose into oxygen and water even at ordinary temp. Speed of decomposition is enhanced by heat, by contact with rough surfaces, dust particles, manganese dioxide, powdered platinum etc.
Reaction with litmus soln.	Does not change the colour of the indicator. (neutral)	Feebly acidic, when pure, it turns blue litmus red.
Action on metals	Causes mercury to lose its mobility and shining appearance When slightly heated, silver is blackened	No action on mercury.
Oxidising property	Possesses powerful oxidising properties, liberates iodine from potassium iodide solution.	Powerful oxidising agent, oxidises potassium iodide to iodine.
Reducing property	Acts as a reducing agent in certain reactions $\text{H}_2\text{O}_2 + \text{O}_3 = \text{H}_2\text{O} + 2\text{O}_2$ $\text{BaO}_2 + \text{O}_3 = \text{BaO} + 2\text{O}_2$	Exhibits reducing property in certain reactions $\text{Ag}_2\text{O} + \text{H}_2\text{O}_2 = 2\text{Ag} + \text{H}_2\text{O} + \text{O}_2$
Bleaching property	Bleaches indigo by oxidation.	Bleaches wool, silk, feather etc. by oxidation.
Reaction with KMnO_4 soln. acidified with dil H_2SO_4	No reaction.	Pink colour of the solution is discharged.
KI Soln + FeSO_4 Soln.	Does not liberate iodine	liberates iodine.

Property	Ozone	Hydrogen peroxide.
K_2CrO_4 Soln. + dil H_2SO_4 + ether	No reaction	Ether-layer turns deep blue.
Titanium dioxide + dil. H_2SO_4	No reaction	Orange yellow colour develops.
Paper soaked in manganous chloride soln.	Paper turns brown	No change of colour.
Paper soaked in alcoholic soln. of benziline	Paper turns brown	No change of colour.
Formation of addition compounds	Forms addition products with unsaturated compounds $C_2H_4 + O_3 = C_2H_4O_3$	Forms addition compounds with both inorganic and organic substances. KF, H_2O_2 ; $CO(NH_2)_2$ H_2O_2

CHAPTER 2

AIR AND NITROGEN

The atmosphere is the gaseous mixture which envelops the earth and in which we live. It is commonly called the 'air'. The ancient philosophers used the term 'air' in the sense we use the word 'gas' and regarded it as an element. Mayow (1674) was probably the first to put forward reliable evidence for the composite nature of air. He showed that the volume of the air is diminished due to breathing of a mouse confined in a bell-jar over water. He arrived at the same result by burning combustible substances under similar conditions. It was also observed that the residue of gas left after these experiments did not support combustion and was unsuitable for breathing. The presence of carbon dioxide in the air was established by Black (1755) who called it *fixed air*. However, Lavoisier proved conclusively that air was a mixture of gases and not an element.

Constituents of air.

Lavoisier's famous experiments on the composition of air :

In 1775, Lavoisier proved experimentally that air consisted of two gases, an active gas and an inert gas. He also determined the ratio between these two gases by volume in air.

Lavoisier's experiment with mercury :

Lavoisier took a weighed quantity of pure mercury (4 ounces) in a glass retort, the long neck of which was in communication with a measured volume of air in a graduated bell jar kept inverted over mercury. At first, the surface of mercury inside and outside the jar was in the same level and the volume of air inside the bell jar was noted. The retort was then heated in a furnace at a temperature near the boiling point of mercury. During heating, red scales were

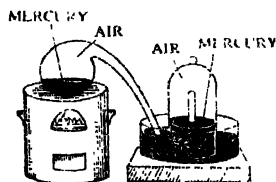


Fig 2(29) Lavoisier's experiment with mercury

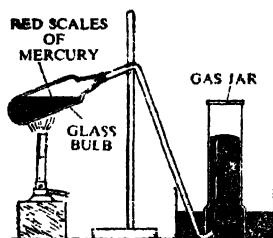


Fig 2(30) Lavoisier's reverse experiment

formed and found floating on the surface of mercury. The level of mercury gradually began to rise up in the jar indicating the diminution in volume of air inside. When, after 12 days, no more red scales appeared to be forming and the mercury level seemed to be steady, Lavoisier stopped heating. The unchanged residual volume of the air was measured when cold and was found to occupy about four-fifths of the air originally taken, i.e. nearly one-fifth of the vol. of air was absorbed by heated mercury.

The flame of a burning candle was extinguished when introduced in the residual air in the jar. Moreover, a mouse died of suffocation when placed in the gas. Lavoisier realised that the residual air did

not support combustion or respiration. He called the gas 'azote' which was afterwards given the name nitrogen.

Lavoisier's experiment with the red scale :

Subsequently, Lavoisier performed the reverse experiment.

He carefully collected the solid red scales formed in the previous experiment and took them in a retort having a drawn-out long bent delivery tube. The free end of the delivery tube was put under mercury and a graduated gas jar filled with the same metal was inverted over it. On strongly heating the scales, a colourless gas was evolved which was collected by the displacement of mercury. The residue left in the retort was metallic mercury. The volume of the gas liberated was found to be exactly equal to the diminution in volume of the air in the bell jar. Thus, the volume of air absorbed by mercury in the first experiment was equal to the volume of air given off in the second experiment. A burning candle continued to burn more energetically in the gas. The gas was also found to support respiration of a mouse placed in it.

This gas was first called 'vital air' and afterwards oxygen by Lavoisier. It occupies one fifth of the air by volume. When this oxygen was mixed with the residual air (i.e. nitrogen) in the bell jar, there was no thermal change and a gas indistinguishable from ordinary air was produced.

From these two experiments, Lavoisier came to the following conclusions :

(i) *Air is a mixture of two gases of different nature. One of the gases is oxygen and the other nitrogen (azote). Oxygen is very reactive but non inflammable. Oxygen of the air supports combustion and respiration and combines with metals during calcination. Nitrogen, on the other hand, is comparatively inert and is not a supporter of combustion or respiration.*

(2) *Air contains oxygen and nitrogen approximately in the ratio of 1 : 4 by volume.*

Why did Lavoisier, out of all substances, select mercury as the starting material in his famous Bell-jar experiment ?

During his experiments on combustion in 1772, Lavoisier observed that the metal when calcined increased in weight and an equal volume of air was absorbed. Moreover, in a given volume of air, calcination proceeded only to a fixed limit and an unabsorbed residual gas remained.

In August 1774, Priestley heated some calx of mercury (i.e. the substance left when mercury is burnt) in a small dish floating on mercury under a bell-jar, by means of the sun rays concentrated by a lens. He obtained a new gas with very striking properties. The gas allowed a candle to burn in it vigorously.

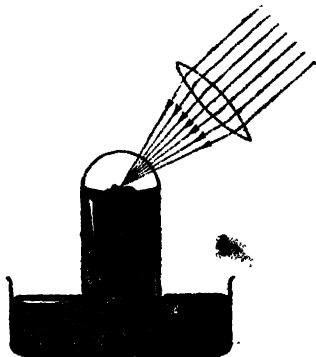


Fig. 2(30A) Priestley's experiment.

In October 1774, Priestley met Lavoisier and described to him this wonderful gas and how he had obtained it. Lavoisier at once grasped the significance of Priestley's discovery and realised that calx of mercury was formed with an increase in weight by heating mercury in air. With a view to showing that the new gas was the part of the air absorbed when metals were calcined, Lavoisier devised his best known Bell-jar experiment and selected mercury as the starting material.

The volumetric composition of air can also be determined by the following method.

Burning of phosphorus in a bell-jar : A small porcelain crucible containing a piece of yellow phosphorus is allowed to float on water in a glass vessel. A bell-jar fitted with a stopper is placed over the crucible. The surface of water inside and outside the bell-jar should remain in the same level. The bell-jar above the water-level is graduated into five equal portions. The phosphorus is then ignited with the help of a hot long iron needle and

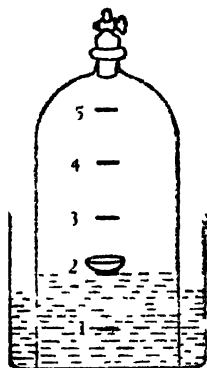
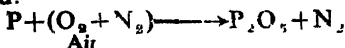


Fig 2(31) Burning of phosphorus in a bell-jar

the stopper is quickly inserted. The phosphorus burns with a bright yellow flame giving off dense white fumes. After a time, the phosphorus no longer burns. The water level inside the bell-jar is found to rise up gradually and when the jar is cold, the water-level stands at the mark which indicates one-fifth of the volume of air. The remaining four-fifths are filled with the residual gas which does not support combustion of phosphorus. If a lighted taper is introduced into it, the taper is extinguished. Therefore, the residual gas is nitrogen. From this experiment, it is proved that oxygen constitutes about one-fifth of the air by volume and nitrogen about four-fifths. This method may also be used for the preparation of nitrogen from air.

During combustion, phosphorus combines with the oxygen of the air forming phosphorus pentoxide which reacts with water to give soluble phosphoric acid. Thus, the oxygen of the air is removed.



The average proportion of the constituents of air

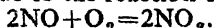
Air is chiefly a mixture of oxygen and nitrogen. Besides these two gases, air contains water vapour, carbon dioxide and the inert gases helium, neon, argon, krypton, xenon etc. in very small quantities. The average composition of air is given below :

Nitrogen	77.16% by volume
Oxygen	20.60% " "
Carbon dioxide	1.40% " "
Water vapour	0.04% " "
Inert gases	0.80% " "

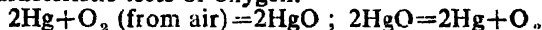
As air is a mixture, its composition varies to a small extent from place to place and from time to time. Minute traces of ozone, ammonia, vapours of nitrous and nitric acids, sulphur dioxide, hydrogen sulphide are found present in air.

Detection, function and constancy of the constituents of air :

Oxygen : (a) when a jar of nitric oxide (a colourless gas) is exposed to air, reddish brown fumes of nitrogen dioxide are produced due to the reaction of nitric oxide with oxygen.



(b) When mercury is heated near its boiling point in air for a long time, mercury absorbs oxygen and red scales of mercuric oxide are obtained. The red scales on being strongly heated decompose into the liquid mercury and a colourless gas which responds to the characteristic tests of oxygen.



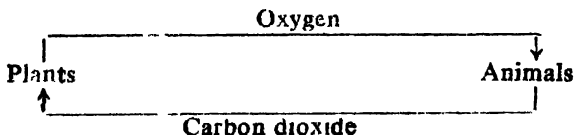
The above experiments prove that air contains oxygen.

Function : Oxygen is absolutely necessary for all living creatures for their respiration. During breathing, oxygen enters into the lungs and slowly oxidises the various complex organic substances inside the body with the simultaneous liberation of heat. Heat thus evolved provides energy and maintains the warmth of the body.

Moreover, oxygen brings about oxidation of many substances on the earth and is absolutely essential for all types of combustion.

Constancy : We know that respiration is a combination of two processes--inhalation of oxygen and exhalation of carbon dioxide. Human beings and other animals inhale atmospheric oxygen which oxidises the tissues of body producing carbon dioxide. The carbon dioxide thus formed is exhaled. Besides respiration, oxygen of the air is consumed during the combustion of fuels such as coal, wood etc and other substances with liberation of carbon dioxide in the air. If these processes of respiration and combustion go on continually, the amount of oxygen in the air should decrease and that of carbon dioxide increase to a large extent. But the oxygen content of the air is practically constant. This is due to a cyclic process occurring in nature called oxygen-carbon dioxide cycle.

The green plants take up carbon dioxide from the air and convert it to their food materials by the process known as photosynthesis with the simultaneous release of oxygen in the air. The consumption of atmospheric oxygen by respiration and combustion and liberation of oxygen into the atmosphere by the way of photosynthesis occur in the nature in such a way that the proportion of oxygen in the air is maintained constant.



Nitrogen : The residual gas left after the removal of oxygen of the air by heated mercury (Lavoisier's expt) or combustion of phosphorus in the bell-jar is nitrogen (together with the inert gases). The gas does not support combustion. If a lighted taper is plunged into it, the taper is extinguished. Moreover, the gas is completely absorbed by strongly heated magnesium. These experiments prove that the air contains nitrogen.

Function : The most important function of nitrogen of the air is to dilute oxygen. If there were no nitrogen, oxidation and combustion would take place very rapidly. Nitrogen moderates the processes of oxidation, combustion and respiration by reducing the intense activity of oxygen. Nitrogen of the air is indirectly utilised in building the complex nitrogenous compounds known as proteins which are absolutely necessary for plant and animal lives.

Constancy : The proportion of nitrogen in the air is practically fixed. Detailed discussion about the constant proportion has been given later.

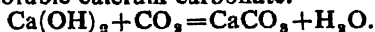
Water vapour : (a) A few pieces of ice are taken in a glass beaker outside of which is completely dry. After some time, minute drops of a liquid are found to appear at the outer surface of the beaker. This liquid is nothing but water as it turns white anhydrous copper sulphate blue. The water vapour present in the air condenses in contact with the cold surface of the beaker and appears as droplets of water.

(b) The presence of water-vapour in the air may also be demonstrated by exposing some anhydrous calcium chloride on a watch glass to the air. The substance on the watch glass soon becomes moist owing to the absorption of water vapour of the atmosphere and ultimately a solution of the compound is obtained after a day or two. If the solution is distilled, the colourless liquid obtained may be proved to be water by the usual tests mentioned earlier. These experiments prove the presence of water vapour in the atmosphere.

Functions : Water vapour in the atmosphere serves the function of controlling the evaporation of water from the surface of the earth. It condenses to clouds at the upper atmosphere and the condensed water ultimately descends to the earth as rains which are essential for the plant and animal lives.

Constancy : About $\frac{3}{4}$ ths of the surface materials of the earth consist of water. Under the influence of the sunrays, water on the crust of the earth evaporates to form water vapour in the air. This water vapour, on the other hand, condenses into clouds in the cooler upper region of the atmosphere and returns to the earth in the form of rains, snow etc. The processes of evaporation and condensation occur in the nature in such a way that the reservoirs of water do not become completely dry and the amount of water vapour in the air varies within a reasonable limit.

Carbon dioxide : The presence of carbon dioxide in the air may be shown by a simple experiment. A little lime water is taken in a shallow dish and is exposed to the air. After some time, the clear lime water is covered with a white crust and will gradually go turbid due to the absorption of carbon dioxide of the air and formation of insoluble calcium carbonate.



Function : The green plants prepare their chief food materials from the carbon dioxide of the air by the process of photosynthesis.

The constancy in proportion of carbon dioxide in the atmosphere has been explained in the chapter 4 during the discussion of carbon dioxide cycle.

Air is a mechanical mixture and not a chemical compound.

The evidences in support of the fact that air is a mixture and not a compound are summarised below.

(1) The proportion of nitrogen and oxygen in the air by weight is very nearly but not entirely constant. Slight variations in composition are observed when samples of air from different localities and at different times are analysed. The composition of a compound is always fixed and definite. No compound is known to have a variable composition.

(2) The elements in air are not present in simple atomic ratios and the composition of air corresponds to no simple chemical formula such as it would be expected to possess if it were a compound.

(3) The density of air as determined experimentally is 14.4 which corresponds to a mixture of nitrogen and oxygen roughly in the ratio of 4 : 1 by volume. If air were a compound, its formula as may be arrived at from its percentage composition would be N_4O (or more accurately N_{15}O_4) and its vapour density would be 36 (or 137).

(4) Ordinarily, nitrogen and oxygen are present in the air in the ratio of 4 : 1 by volume. When air is dissolved in water and the solution is boiled out again to expel the dissolved air, it is observed that the expelled air contains greater percentage by volume of oxygen than undissolved air. The proportion of nitrogen and oxygen by volume in the dissolved air is nearly 2 : 1 as against 4 : 1 in ordinary air. This is merely due to the fact that oxygen is more soluble in water than nitrogen.

If air were a compound, its composition could not be altered by simply dissolving in water.

(5) The characteristic properties of nitrogen and oxygen are retained in the air although the chemical reactivity of oxygen is decreased to some extent due to the presence of inert nitrogen in air.

If air were a compound of nitrogen and oxygen, it would possess properties entirely different from either of the two elements.

(6) If nitrogen and oxygen are mixed in appropriate proportion as they are present in air, there is no absorption or evolution of heat, volume change or other evidence of chemical combination but the mixture resembles ordinary air in every way. If air were a compound, there would inevitably be a thermal change during its formation from its constituent elements.

(7) As air is a mixture, its constituents may be separated by simple physical means such as vaporization, diffusion etc.

(a) When liquid air is allowed to evaporate, nitrogen evaporates more quickly leaving almost pure oxygen. If air were a compound, it would evaporate unchanged in composition at a fixed temperature.

(b) If air is passed through a porous tube of unglazed porcelain, nitrogen being lighter than oxygen diffuses out more rapidly than oxygen. The diffused air becomes richer in nitrogen and the air inside the tube contains greater percentage of oxygen. Had air been a compound, no variation in its composition would be observed during diffusion.

NITROGEN

Symbol N.	Atomic number 7
Molecular formula N_2	Electronic configuration $1s^2 2s^2 2p^2$
Atomic weight 14.08	Position in periodic table VB

Nitrogen was discovered by Daniel Rutherford in 1772. Its elementary nature was proved by Lavoisier who called it 'azote' meaning non-supporter of life. The name nitrogen was given by Chapal in 1790 as it is present in nitre.

In the free state, nitrogen occurs in the air and constitutes about four-fifths of its volume. In the combined state, it is present in plants and animals in the form of complex proteins. More over, it is found in ammonia, nitre or potassium nitrate, and Chile saltpetre ($NaNO_3$), a mineral deposit in Chile.

Preparation of nitrogen : Nitrogen is prepared from the compounds containing nitrogen or from air by removal of oxygen.

1. (A) By the action of heat on ammonium nitrite :—

Laboratory method : Nitrogen is prepared in the laboratory by slightly warming a concentrated solution of ammonium nitrite. Thermal decomposition of ammonium nitrite may take place with explosion. So, instead of ammonium nitrite alone, a concentrated solution containing equimolecular quantities of ammonium chloride and sodium nitrite is heated slowly. Ammonium nitrite, initially formed by double decomposition of the two salts, decomposes into nitrogen and water.



A concentrated solution of sodium nitrite and ammonium chloride (1 : 1) is taken in a round bottomed flask fitted with a

thistle funnel and a bent delivery tube. The end of the thistle funnel is always kept under the surface of the liquid in the flask and the outer end of the delivery tube dips under water in a trough. The solution in the flask on slight warming liberates nitrogen which comes out through the delivery tube. After allowing the gas to escape for some time in the form of effervescence, a gas jar completely filled with water is now inverted over the end of the delivery tube. Nitrogen collects in the jar by the downward displacement of water.

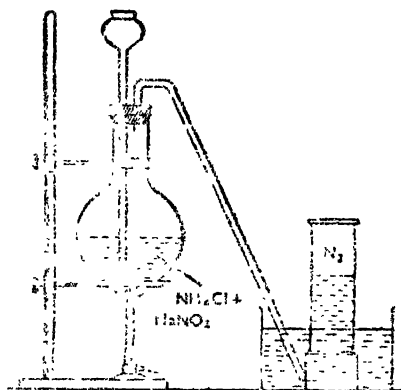


Fig. 2(32) Preparation of nitrogen in the laboratory.

If the reaction proceeds rapidly, the flask is cooled and if the evolution of gas ceases, the flask is gently warmed.

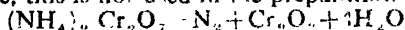
Purification: Nitrogen obtained by this method is liable to contain a little oxides of nitrogen, chlorine, ammonia and water vapour as impurities.

The gas is first passed through a solution of caustic potash to absorb chlorine and then through conc. sulphuric acid to remove ammonia and moisture. On passing the gas through a red hot tube containing copper turnings, the oxides of nitrogen present are reduced to nitrogen $2NO + 2Cu = 2CuO + N_2$.

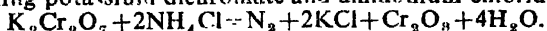
Nitrogen, thus purified, is collected over mercury.

Precautions: The flask is to be heated slowly and carefully. Instead of heating directly, it is better to heat the flask on a water bath. The reaction may occur violently if the solution of ammonium nitrite is heated strongly. Source of heat should be removed as soon as nitrogen begins to evolve. The flask is subjected to cooling if the reaction proceeds vigorously.

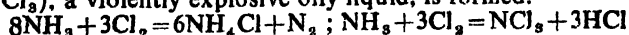
(B) Ammonium dichromate, on slight heating, decomposes producing nitrogen. As the decomposition takes place with explosive violence, this is not used in the preparation of nitrogen.



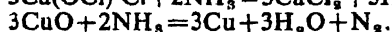
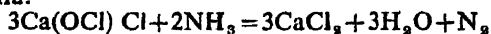
The reaction becomes less vigorous if a concentrated solution containing potassium dichromate and ammonium chloride is used.



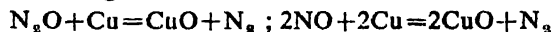
(C) **Nitrogen from ammonia:** When chlorine is passed through a strong ammonia solution, ammonia is oxidised to nitrogen. Ammonia must be in large excess, otherwise nitrogen trichloride (NCI_3), a violently explosive oily liquid, is formed.



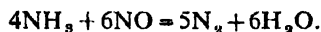
Bleaching powder or heated copper oxide liberates nitrogen from ammonia.



(D) **From oxides of nitrogen :** Nitrous oxide (N_2O), nitric oxide (NO) etc. when passed over heated metallic copper are reduced to nitrogen.

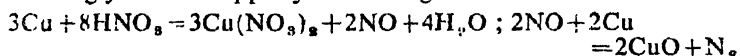


Pure nitrogen can be obtained by passing a mixture of nitric oxide and ammonia in right proportion over heated copper powder.

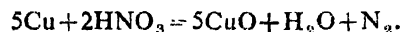


The gas is dried by conc. sulphuric acid and collected over mercury.

(E) **From nitric acid :** Moderately strong nitric acid, on being treated with metallic copper, forms nitric oxide, which when passed over strongly heated copper yields nitrogen.



Nitrogen can also be obtained from nitric acid by passing the vapour of the acid through a strongly heated tube containing copper.



(2) (A) **Nitrogen from air :** Air is mainly a mixture of nitrogen and oxygen approximately in the proportion of 4 : 1 by volume. Nitrogen may be obtained by simply removing oxygen from the air. Removal of oxygen may be achieved by application of different methods.

(a) **Removal of oxygen from air by means of phosphorus :**

This method has already been described in connection with the composition of air. It is to be noted that the complete removal of oxygen from air is not possible by this method.

(b) **Removal of oxygen from air by red-hot copper :**

A long hard glass tube containing some copper filings is placed horizontally in a furnace.

One end of the tube is connected with an inlet tube for entry of oxygen and the other end is provided with a delivery tube the free end of which dips under water as in Fig 2(33).

The combustion tube is then strongly heated and a slow stream of air freed from carbon dioxide and moisture is passed over the heated copper in the tube. At the high temperature, oxygen of air combines with copper to form black cupric oxide which remains in the tube and the unchanged nitrogen gas passes out through the delivery tube and is collected over water. $2\text{Cu} + \text{O}_2 = 2\text{CuO}$.

(B) Nitrogen from liquid air : Nitrogen is obtained in industry by the fractional distillation of liquid air. The process of liquefaction of air and the subsequent separation of nitrogen and oxygen have been described earlier in connection with the preparation of oxygen from air.

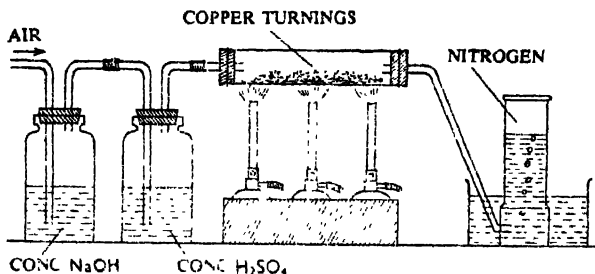


Fig. 2(33) Preparation of nitrogen from air.

The density of nitrogen obtained from air slightly differs from that of nitrogen prepared from its compounds. Experimental results are shown below.

Density of nitrogen obtained from air = 1.2572
and " " " " its compounds = 1.2506

Besides nitrogen, oxygen, carbon dioxide, water vapour, air contains some inactive gases like helium, argon, krypton, neon, xenon etc in minute traces (about 0.8% by volume). Due to their chemical inactivity, these gases do not combine with other substances. So, nitrogen obtained from air after removal of oxygen, carbon dioxide, moisture is not free from these inert gases each of which (except helium) is slightly heavier than nitrogen. This is why the density of nitrogen from air is slightly greater than that of nitrogen prepared in the pure state from its compounds.

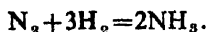
Properties—Physical : (1) Nitrogen is a colourless gas without any smell or taste. (2) It is slightly lighter than air (vapour density = 14; H = 1) (3) Gaseous nitrogen molecule is diatomic (4) It is almost insoluble in water. (5) On cooling under suitable pressure, it can be condensed to a liquid and subsequently frozen to a solid (b.p. of liquid nitrogen = -195.8°C and freezing point of solid nitrogen = -209.86°C). (6) It is non-poisonous but does not support respiration. Hence, an animal cannot live in the gas.

Chemical: Ordinarily, nitrogen is an inert gas. At ordinary temperature, it does not react with other elements or compounds but its reactivity increases at higher temperatures.

(1) It is neither combustible nor a supporter of combustion.

(2) Nitrogen enters into chemical combinations with many non metals at higher temperatures.

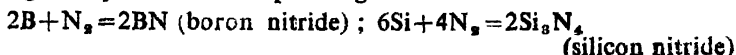
(a) Under high pressure (200 atm) and at a temperature of about 550°C, nitrogen combines with hydrogen to produce ammonia.



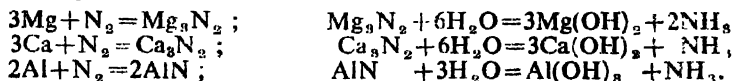
(b) Under the influence of electric sparks, nitrogen and oxygen combine at about 3000°C forming nitric oxide. With excess of oxygen, nitrogen dioxide is formed.



(c) At red heat, non-metals like boron, silicon etc. unite with nitrogen to yield the corresponding nitrides.



(d) Nitrogen combines with heated metals like magnesium, calcium, aluminium to form the respective metallic nitrides which undergo hydrolysis on boiling with water to give ammonia and the metallic hydroxides.



(e) Heated calcium carbide absorbs nitrogen at about 1100°C forming calcium cyanamide. Carbon is also produced as a result of the reaction.



— Calcium carbide

Calcium cyanamide

The brown mixture of calcium cyanamide and carbon thus obtained is commercially known as nitrolim. It is used as a fertilizer.

Calcium cyanamide is hydrolysed by super heated steam to produce ammonia and calcium carbonate.

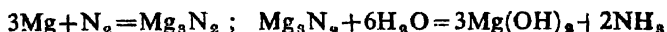


Experiments to illustrate some of the properties of nitrogen :

(1) *Nitrogen does not support respiration* (i) A mouse is introduced into a gas-jar full of nitrogen. The mouth of the jar is closed by a lid. After some time, the animal dies of suffocation.

(2) *Nitrogen is not combustible and ordinarily not a supporter of combustion.* A lighted taper is introduced into a jar of nitrogen. The gas does not burn and the taper inside is extinguished.

But it supports the combustion of burning magnesium. A piece of burning magnesium ribbon is plunged into a jar of nitrogen with the help of a pair of tongs. Magnesium is not extinguished but continues to burn producing a white powder. This white residue when boiled with water gives off ammonia which turns red litmus blue and Nessler's solution brown.



Uses : (1) It is used in the manufacture of ammonia, nitric acid and nitrolim, a nitrogenous fertilizer. (2) It is also used in making gas-thermometers and for filling some electric bulbs (3) It finds its application in creating inert atmosphere in some chemical processes. (4) Liquid nitrogen is used as a refrigerant.

Tests : At ordinary temperature, nitrogen is so inert that no positive test can be applied. We can only show that a given gas is nitrogen by elimination of other possibilities.

- (1) It is a colourless gas which extinguishes a lighted taper.
- (2) It does not turn lime water milky
- (3) It is without action upon strongly heated copper.
- (4) Nitrogen is absorbed by heated magnesium and the product on boiling with water gives off ammonia.

Comparison of the properties of nitrogen and oxygen.

Oxygen	Nitrogen
Colourless, odourless, tasteless gas.	Colourless, odourless, tasteless gas.
Slightly heavier than air.	Slightly less dense than air.
Slightly soluble in water.	Almost insoluble in water.
Not inflammable but is a supporter of combustion.	Not inflammable, ordinarily does not support combustion.
Very active element, can support respiration.	Inactive element, does not support respiration at all.
Absorbed by alkaline potassium pyrogallate solution at ordinary temperature.	Under ordinary conditions, it has no absorbent.

It is found that sulphur, carbon, phosphorus etc. burn more brilliantly in pure oxygen than in air. This happens because oxygen in the air is diluted by nitrogen which reduces the activity of oxygen and intensity of combustion.

The nitrogen cycle : Nitrogen plays a very important role in the life processes of plants and animals. It is an essential constituent of the class of complex organic compounds known as proteins which are absolutely necessary as nitrogenous food materials for all living organisms.

In the free state, nitrogen occurs in the atmosphere to the extent of about 78% by volume. Ordinary nitrogen is comparatively an inert element and with the exceptions of a few leguminous plants, no plant or animal can assimilate nitrogen of the air directly. The elementary atmospheric nitrogen enters into the life processes of plants and later of animals through some natural processes stated below

- (1) Certain leguminous plants like peas, beans, grams always have colonies of symbiotic bacteria on the nodules of their root-hairs. These bacteria are capable of converting atmospheric nitrogen directly into compounds which are taken up by plants. There are some algae and fungi which can also utilise nitrogen of the air. But the number of such plants is limited and only a very small quantity of nitrogen can thus be fixed. Almost all the plants secure the necessary nitrogen indirectly from the nitrates (or nitrites)

and ammonium salts present in the soil or supplied to it in the form of nitrogenous fertilizers.

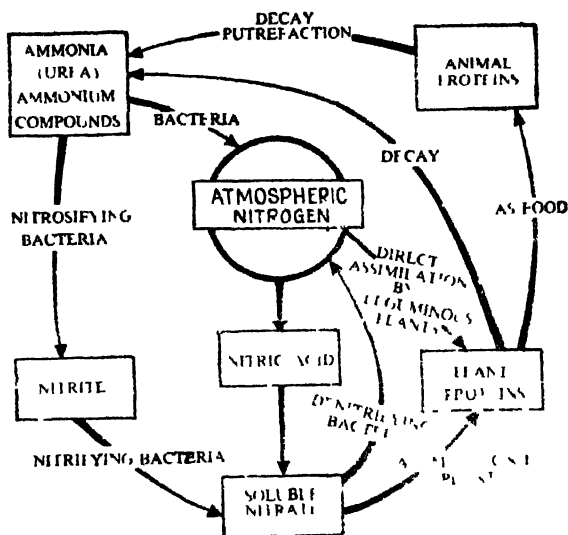
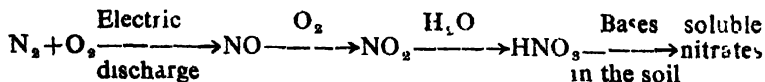


Fig. 2(34) Nitrogen cycle

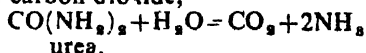
(2) During electric discharge (lightning) in the upper atmosphere, a portion of nitrogen and oxygen of the air combine chemically to produce nitric oxide. This oxide is further oxidised by the atmospheric oxygen into nitrogen dioxide which reacts with rain water forming nitric acid. The acid thus formed is washed down by rains to the soil where it is converted into soluble nitrates by reacting with the bases present. These soluble nitrates from the soil are absorbed by the plants through their roots and are ultimately transformed into proteins which are vitally important for the maintenance of plant lives. This is the main process of nitrogen-assimilation by the plants.



Animals on the other hand are totally unable to assimilate nitrogen directly either from the air or from the soluble nitrates present in the soil. Herbivorous animals get their supply of proteins from the plants which they eat. Carnivorous animals consume proteins of other animals. Human being can receive the proteins from both plants and other animals using them as food.

As a result of the above processes of continual utilisation of atmospheric nitrogen by the living world, the nitrogen content of the air should gradually decrease. But this is never observed. In fact, the proportion of nitrogen in the air always remains practically constant. This is possible as the air receives back free nitrogen from the nitrogenous compounds of plant and animal origins by some opposite processes simultaneously taking place in nature.

Major part of nitrogen consumed by the animals is excreted and returned to the soil in the form of urea which is readily hydrolysed to ammonia and carbon dioxide,



Moreover, ammonia is liberated in the soil by the decay and putrefaction of dead plants and animals. Ammonia thus formed as a result of decomposition of the organic nitrogenous compounds (proteins) present in the decaying plants and animal bodies is first oxidised in the soil to nitrites by the nitrosifying bacteria and then to nitrates by the nitrifying bacteria. These nitrates are partly assimilated by the plants and are partly restored to the atmosphere as free nitrogen by the action of denitrifying soil bacteria.

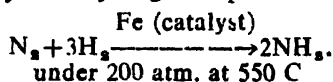
Thus, the natural processes of conversion of atmospheric nitrogen into proteins necessary for life processes of plants and animals and the release of free nitrogen into the air by the decomposition of such nitrogenous compounds take place in a cyclic way and this cycle is termed as Nitrogen Cycle. The two opposite processes mentioned above occur in the nature in such a way as to maintain the nitrogen content of air almost fixed. Thus, nitrogen undergoes an evercontinuing cycle which maintains a state of balance in the atmosphere.

Fixation of atmospheric nitrogen : The conversion of nitrogen of the air into useful nitrogenous compounds by any natural or artificial process is known as the fixation of atmospheric nitrogen.

It has already been stated that some leguminous plants always have colonies of bacteria on their roots which are able to transform nitrogen of the air directly into its compounds. Moreover, as a result of electric discharge (lightning) in the upper atmosphere, some nitrogen and oxygen may combine together yielding nitric oxide. This oxide on being reacted with atmospheric oxygen is converted into nitrogen dioxide. The dioxide with rain water gives nitric acid which is carried down into the soil. The acid reacts with the basic substances of the soil and is ultimately transformed into nitrates which are then assimilated by the plants. The percentage of nitrogen fixed by the natural processes is very small. Besides, most of the nitrogen compounds obtained by these processes are lost into the sea and thus becoming unavailable for direct use of the plants. In order to increase the available nitrogen content in the soil, various nitrogenous fertilizers are nowadays used. Hence, the necessity of fixing atmospheric nitrogen by artificial methods has been felt.

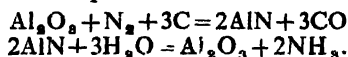
The important artificial processes by which nitrogen of the air can be fixed as valuable substances like ammonia, nitric acid, and various manures are stated below.

(1) *Haber's process*: In this process, nitrogen of the air combines directly with hydrogen to produce ammonia.



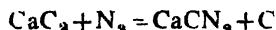
Ammonia can be easily converted into various ammonium salts and urea which are commonly used as fertilizers. Ammonia can also be employed as a source for large scale production of nitric acid.

(2) *Serpch's process*: In this process, a mixture of aluminium oxide (alumina) and coke is heated in a current of air at about 1500°C . when aluminium nitride is produced. This nitride on being hydrolysed with steam produces ammonia.



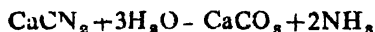
This method is practically obsolete.

(3) *Cyanamide process*: In this process, calcium cyanamide is obtained by heating calcium carbide in a current of nitrogen at high temperature.



The dark grey product which is a mixture of calcium cyanamide and carbon is directly used as a fertilizer under the trade name 'nitrolim'.

Calcium cyanamide may be used for the industrial preparation of ammonia.



This process cannot be widely applied in countries where electrical power is not cheap.

(4) *Birkeland and Eyde process*: Nitrogen and oxygen of the air are made to combine with each other to form nitric oxide at the high temperature (about 3000°C) produced by means of an electric arc. This oxide can easily be converted into nitric acid. At present, this process finds limited application.

The methods mentioned above will be discussed in detail in different chapters of this book.

CHAPTER 3

THE NON-METALS

CARBON, PHOSPHORUS, SULPHUR & HALOGENS

CARBON

Symbol C

Atomic no 6

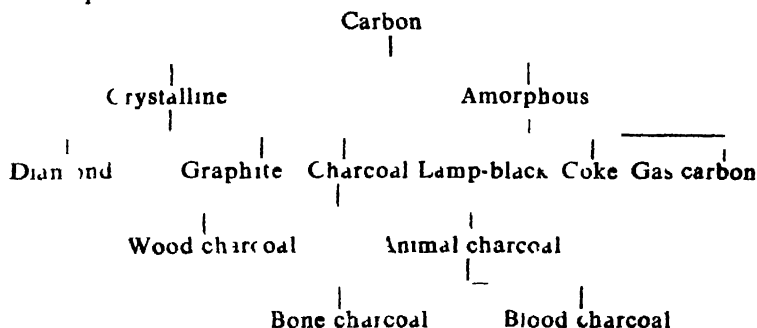
Atomic weight 12.00

Electronic configuration $1s^2 2s^2 2p^2$

Position in periodic table IV B

Carbon is found in nature in the free state and also in the form of various compounds. Elementary carbon occurs in nature in the crystalline form as diamond and graphite. Coal contains but does not consist of free carbon. Coal is a complex carbonaceous mineral substance of dark brown or black colour. This is regarded as the final product of slow decomposition of the dense pre-maeval forests buried under the earth's surface in the remote past as a result of earthquakes and similar natural processes. In course of time these vast forests under the influence of high pressure and temperature in the interior of earth and several bacteria present there underwent various chemical transformations and ultimately mummified into coal. In combination with other elements carbon is found in vast quantities as carbonates, mineral oils and organic matter of all kinds. It also occurs in the air to a small extent (0.02-0.04% by volume) as carbon dioxide.

Allotropy of carbon Carbon exhibits allotropy. It exists in both crystalline and amorphous allotropic forms. The crystalline form includes diamond and graphite and the amorphous form includes charcoal, lamp black, coke, gas carbon etc. In spite of having distinct difference in structures and properties, the different forms of carbon consist of the same element. The different allotropic forms are classified as follows:



N.B. Recent X-ray studies on the structures of charcoal, coke, and many other varieties of so-called amorphous carbon have definitely proved that they consist of micro-crystals of graphite. Thus in the light of these observations only two true crystalline allotropic forms of carbon are recognised. The apparent non-crystalline structure of the amorphous varieties is due to the fact that these micro-crystals are not uniformly distributed or arranged in them. In other words, the micro-crystalline particles are haphazardly oriented in the mass of the amorphous material.

Crystalline allotropes of carbon

Diamond Diamond occurs naturally in South Africa, Brazil, New South Wales and in Goleconda in India. On account of its

beauty, rarity and permanence of properties, diamond is prized as a very valuable gem. Like other precious stones, diamond is expressed in carots,* (1 carot = 0.20 gm). The world famous Indian Kohinoor originally weighed 186 carots. Some other precious diamonds are Cullinan (3032 carots), Hope (44.5 carots) and Pitt (136.2 carots).

Extraction: Diamonds are found in alluvial deposits mixed with peculiar type of rock and in river gravels. These substances containing diamonds are left exposed to the weather when they fall to powder. A part of diamonds is first separated by hand picking. The remaining powder mixed with water is led over boards coated with grease or wax. The diamonds adhere to the grease (or wax) and the clay and other impurities pass on with the water. In this way, diamonds are recovered.

Artificial diamond: Artificial diamond was prepared by Moissan in 1896 by heating a mixture of pure iron and sugar charcoal in a graphite crucible in the electric arc furnace to about 3000°C. The whole mass melted and at this high temperature, iron dissolved a good deal of carbon. The crucible was then immersed in molten lead under high pressure and was allowed to cool suddenly. On rapid cooling, the molten iron began to solidify. This resulted in an enormous pressure on the dissolved carbon due to the contraction of iron on solidification. A portion of the dissolved carbon crystallized out in the form of small crystals of diamond. A part of carbon is converted into graphite. Diamond and graphite are freed from iron by dissolving out the latter with hydrochloric acid. This process could not be utilised for commercial purpose owing to the very fine size of the crystals produced. Besides, the process is very costly.

Properties: Pure diamond is a colourless, transparent, lustrous, crystalline substance having a sp. gr. of about 3.5. Although transparent, diamond is occasionally pink, red, green or blue due to the presence of traces of foreign substances. It is the hardest substance known. It is chemically inactive and does not conduct heat or electricity. It is transparent to Rontgen rays (X-rays) whereas imitation diamond made of glass is opaque to these rays. Thus, X-rays furnish a ready means of identification of real diamond.

Uses: (1) For its amazing lustre, diamond is generally used as a gem. (2) On account of its extreme hardness, it has a commercial value for the manufacture of glass cutters and rock hammers.

The opaque and black diamonds known as 'carbonado' and 'bort' are of no value as gems. These are usually used for drilling rocks and for cutting and polishing other diamonds and stones.

Graphite: The word graphite comes from the Greek word 'grapho' meaning I write. It has been so named because it can mark papers. Graphite (also known as plumbago or black lead) is widely distributed in nature. It is found in the native states in Srilanka, Siberia, Italy, United States and in India. Graphite is also prepared artificially.

Artificial preparation of graphite—Acheson's process: Artificial graphite is manufactured at Niagra Falls in U.S.A. according to Acheson's process in which an intimate mixture of sand and

*The term carot is derived from the carobean, a small weight formerly used by the diamond-merchants of India.

anthracite or petroleum coke is strongly heated to a very high temperature between 3000-3500°C for 20-24 hours in a rectangular electrothermal furnace made of fire bricks. The temperature required is produced by means of electric current passing through two large carbon electrodes placed in the mixture and connected together by a central core of carbon rods. The mixture is kept covered by a layer of sand.

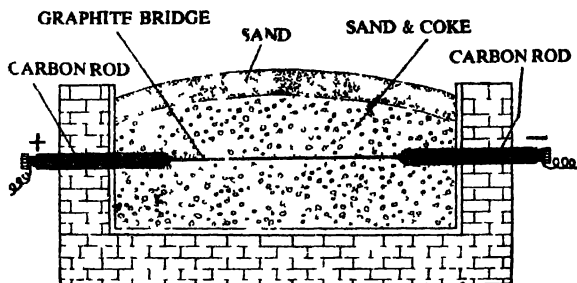
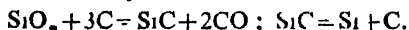


Fig. 2(35) Artificial graphite by Acheson process

At first, sand and carbon react producing silicon carbide which subsequently decomposes at a very high temperature into graphite and elementary silicon. The latter volatilises away.



Graphite is a dark grey, crystalline substance with a sp gr. of 2.2. It is soft, slippery and has a lustre resembling that of a metal. It is a good conductor of heat and electricity.

Uses It is extensively used in the manufacture of lead pencils, as a protective coating for iron articles against rusting and frictions. It is used in making refractory crucibles for use at high temperatures and for making lubricating oil for some machinery parts. Graphite is employed in making electrodes for electric furnaces. Sometimes, non-conducting substances are made conductors of electricity by coating them with a layer of graphite.

It has already been stated that of the two crystalline allotropes of carbon, diamond does not conduct electricity and due to its extreme hardness, it is used as an abrasive. On the other hand, graphite is a good conductor of electricity. It is soft and is used as a lubricant. The difference in properties and uses of diamond and graphite can easily be explained on the basis of the difference in their crystal structures. In the diamond crystal, each carbon atom is covalently linked with four other carbon atoms which are arranged tetrahedrally surrounding it. In this tetrahedral arrangement, carbon atoms are at equal distance from one another. Such a structure extends through out the entire crystal in three dimensions and each crystal of diamond is regarded as a *giant molecule*. The forces acting between the covalently linked atoms are very strong. The lack of electrical conductivity of diamond is due to the complete pairing of all the available electrons so that they

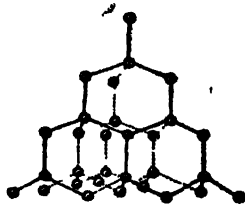


Fig. 2(35A)
Diamond crystal

are firmly held in the carbon-carbon covalent bonds. This particular rigid three dimensional structure also accounts for its extreme hardness, chemical inertness, high melting point and abrasive property since a huge energy is required to break the C-C bonds.

In graphite carbon atoms are situated at the corner of regular hexagons arranged in parallel layers. The distance between the adjacent layers has been found to be greater than that between the adjacent atoms of the hexagon as a result of which the C-C bond between atoms in the same layer is much stronger than that between the layers. In fact, the graphite crystal is itself a giant molecule in two dimensions. This structure with separated layers consisting of a hexagonal net work accounts for the lower density of graphite in comparison to diamond. Since, the layers are relatively loosely bound, they may easily slide over each other. As a result, graphite possesses lubricating property. Three of the valency electrons of each carbon atom in the graphite crystal are involved in forming three covalent bonds with three carbon atoms in the layer. The fourth electrons of the carbon atoms are considerably mobile and hence graphite is a conductor of electricity.

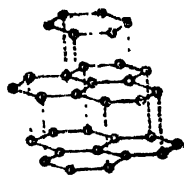


Fig. 2(35B)
Graphite crystal

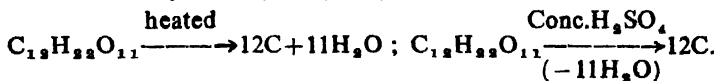
N.B. : It is interesting to note that lead pencil does not contain lead but is made of graphite.

Amorphous carbon—wood charcoal : It is prepared by destructive distillation of air-dried wood in iron retorts. The black, non-volatile solid residue left in the retorts is wood charcoal.

Ordinarily, it is made by burning wood in a limited supply of air in pit or kiln. By this process only 20% of the wood is converted into charcoal and the rest is lost.

Cocoon shells on dry distillation produce wood charcoal.

Sugar charcoal is the purest form of amorphous carbon. It is obtained by destructive distillation of crystalline cane sugar or by the action of strong sulphuric acid on sugar. The resulting charcoal formed as a black mass is washed with water, filtered, dried and heated in a current of chlorine to remove any combined hydrogen in the form of hydrogen chloride. The excess of chlorine is then removed by heating in hydrogen.



Animal charcoal : The residue left in the retorts when small pieces of degreased animal bones are subjected to destructive distillation is called *bone charcoal*. The animal charcoal is a black, coloured, powdered substance having the remarkable property of absorbing colouring matter from solutions. It is not pure and it contains about 80% calcium phosphate along with carbon. This is known as *bone black*. When treated with hot hydrochloric acid, the portion of calcium phosphate dissolves and the dark black charcoal that remains goes by the name of *ivory black*.

Blood charcoal is obtained by destructive distillation of dried blood. It is a superior type of animal charcoal.

Charcoal is a black, soft, amorphous substance having a sp. gr. of 1.4 to 1.9. It is a non-conductor of heat and electricity. It is porous, and though heavier, is found to float on water when dry. This is possible because the large quantity of air present in its innumerable pores reduces the sp. gr. apparently to a lower value of about 0.2.

If the air is expelled from the porous charcoal, it absorbs gases and the absorbed gases remain adhered to the outer surface of it. In this process, the gases are not dissolved in charcoal or do not undergo any chemical reaction with it. Charcoal simply retains the absorbed gases on its surface. The important property by virtue of which the charcoal can take up a gas and retain the same on its surface is termed as adsorption. Obviously, the concentration of the gas taken up is higher at the surface than in any other parts of the charcoal. Generally, adsorption may be defined as a process of existence of higher concentration of a particular substance on the surface of a solid or liquid than is present in the bulk. It is purely a surface phenomenon. The substance upon whose surface the concentration takes place is called the *adsorbent* and the substance which is accumulated on the surface is called the *adsorbate*. The adsorbed gas is released on heating.

Adsorption should not be confused with the term absorption. In the process of absorption, a substance is not only retained on the surface but passes through the surface to become uniformly distributed throughout the body of a solid or a liquid.

The absorptive power of cocoanut charcoal is tremendously increased when it is heated at 900°C in a closed vessel free from air but in the presence of a trace of steam or oxygen. Thus, any specially treated charcoal with enhanced absorbing activity is called activated or active charcoal. Active charcoal may be obtained by the destructive distillation of wood, saw dust etc. previously impregnated with zinc or magnesium chloride solution. Animal charcoal is also a superior type of active charcoal.

Activated charcoal is used as an adsorbent in military and industrial gas masks, for removing the unwanted colours, impurities, odours of liquids. It is extensively used in refining crude sugar since it readily absorbs the colouring matter from the sugar solutions and also for preparation of gun powder. It is also used as a positive catalyst in many chemical reactions at room temperature.

The adsorbed gases are more active than the ordinary gases. Ordinary chlorine does not react with hydrogen in the dark at ordinary temperature. But chlorine adsorbed in charcoal readily combines with hydrogen producing hydrogen chloride even in the dark.

Charcoal is a strong reducing agent. Its reducing power and other properties have been discussed under the chemical properties of carbon.

Uses of charcoal : Wood charcoal is used as a fuel and as a reducing agent in metallurgy. It is often used in filter beds and as

an adsorbent for obnoxious gases. It finds its application in the manufacture of gun powder, in the preparation of activated charcoal which is extensively used in gas masks. In the laboratory, it is used in the charcoal reduction test. Animal charcoal is used in decolouring and purifying sugar. Ivory black is used as a pigment.

Lamp black : It is the purest form of amorphous carbon and is made by burning kerosene, petroleum, terpentine, benzene and other substances rich in carbon in a limited supply of air. The black smoke is then passed into large cold chambers containing suspended coarse blankets upon which the small carbon particles collect as flaky deposits known as soot. This is removed at intervals.

Lamp black is largely used for making printers' ink, shoe-polish and black paints. It is also employed as a filter for rubber.

Coke and Gas Carbon : Coke is the non-volatile solid residue left in the retorts after the destructive distillation of coal. The nature of the coke depends upon the temperature at which the distillation is carried out. If the distillation is conducted at 600–650°C (Low temperature carbonisation), we get soft coke. The coke obtained by high temperature carbonisation (1000–1200°C) is known as hard coke. Gas carbon is a by-product of destructive distillation of coal and is formed as a hard, dense deposit on the upper surface and sides of the retorts.

It is almost a pure form of amorphous carbon and is a good conductor of heat and electricity. Hard coke is used as a fuel and as a reducing agent in metallurgical processes. Soft coke is extensively used as a domestic fuel.

Gas carbon is used in making electrodes in electric furnaces, arc lamps and electric batteries. It is also used in furnace-lining.

Experiment to prove the porosity of charcoal :

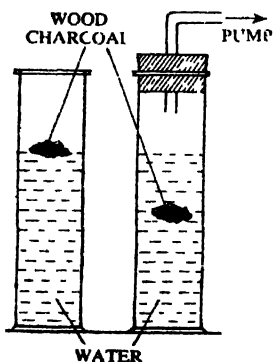


Fig. 2(36) Experiment to prove that charcoal is porous

The sp. gr. of charcoal varies from 1.4 to 1.9. So, it should sink when placed in water. But in practice just the opposite phenomenon is observed.

If a piece of charcoal is placed in a jar containing water, the charcoal instead of sinking is found to float on water. Now, the mouth of the jar is fitted with a cork provided with a glass tube bent at right angle. The outer end of the tube is then connected with an air pump. When the pump is in operation, air escapes from the jar and the pores of the piece of charcoal which gradually begins to sink. It is evident from this experiment that charcoal is porous and the air contained in its pores reduces its effective sp. gr. to a much lower value of 1 (i.e. sp. gr. of water).

Experiment to show that charcoal is a good adsorbent : The power of adsorption of charcoal is illustrated by the following simple experiment.

A glass tube closed at one end is filled with ammonia gas and is inverted over a trough of mercury. A piece of wood charcoal after being heated to expel air from its pores is then introduced in the tube containing ammonia. Charcoal adsorbs ammonia readily and as a result, mercury from the trough rises up and entirely fills the tube.

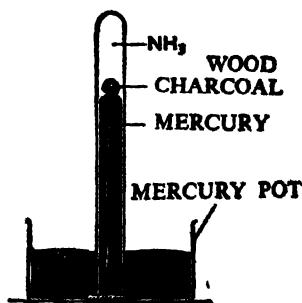


Fig. (37) Adsorption of gases by charcoal

If the same experiment is repeated with chlorine and sulphur dioxide separately, it is found that these gases are also adsorbed by charcoal.

Active charcoal is better adsorbent for gases than ordinary charcoal.

Not only the gases, the animal charcoal is capable of adsorbing the colouring matter from the coloured solutions. Smell or even the taste of a substance is sometimes found to be removed by a suitable charcoal.

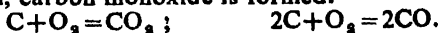
(i) Coloured solution of molasses is decolourised by boiling with animal charcoal.

(ii) A hot red or blue litmus solution on being shaken with animal charcoal becomes colourless. Blue indigo solution after boiling with active charcoal is filtered. The filtrate obtained is found to be colourless.

(iii) If a solution of quinine sulphate is filtered through a bed of activated charcoal, the filtrate becomes tasteless. Here, the charcoal has adsorbed the peculiar bitter taste of quinine sulphate.

When a solution of hydrogen sulphide (H_2S) is added to a solution of lead nitrate, black lead sulphide (PbS) is precipitated. But if the solution of H_2S is filtered through a layer of activated charcoal and the filtrate is added to a lead nitrate solution, no black precipitate is obtained. This is due to the fact that active charcoal adsorbs H_2S from its solution.

Chemical properties of carbon : (1) When burnt in air or oxygen, each of the different varieties of carbon combines with oxygen producing carbon dioxide. As a result of burning in a limited supply of oxygen, carbon monoxide is formed.

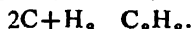


(2) At high temperatures, carbon directly combines with sulphur, nitrogen, hydrogen etc.

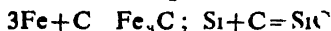
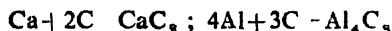


At the elevated temperatures (1100–2100°C) and a pressure of 200 atms, carbon combines with hydrogen forming methane in small quantities. $C + 2H_2 \rightleftharpoons CH_4$.

If an electric arc is generated between the carbon electrodes in the atmosphere of hydrogen, acetylene gas is formed.

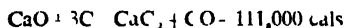


Carbon reacts with heated metals like calcium, aluminium, iron etc. giving the metal carbides. Silicon at very high temperatures, combines with carbon to form its carbide.



Two commercially important carbides are calcium carbide and silicon carbide.

On a commercial scale, calcium carbide is prepared by heating a mixture of 3 parts by weight of lime and 2 parts by weight of coke at a temperature of 2000°C or more in an electric furnace.

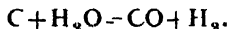


Silicon carbide is commercially made in an electric furnace by heating a mixture of sand and crushed coke (proportion 5 : 3) with some saw dust and a little salt at 1500–2000°C. The commercial (impure) product is normally a dark coloured coarsely crystalline mass having a brilliant iridescent lustre. It is an extremely hard substance commonly known by the trade name carborundum. Since it is fusible with difficulty, it is widely used as an abrasive and as a refractory in furnace linings.

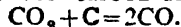
(3) When a limited supply of air is passed through a bed of white hot (temp. 1000°C) coke, the latter combines with the oxygen of the air producing carbon monoxide. The mixture of carbon monoxide and unreacted nitrogen thus formed is known as *producer gas*.

(4) At elevated temperatures, carbon acts as a strong reducing agent. When steam is blown through a bed of white-hot coke at a temperature of 1000°C, the latter reduces steam to hydrogen itself being oxidised to carbon monoxide (a little CO_2 is also formed).

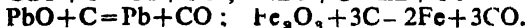
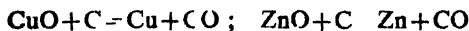
The mixture of equal volumes of carbon monoxide and hydrogen thus produced is known as *water gas*.



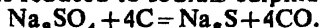
Carbon at red heat reduces carbon dioxide to carbon monoxide.



Carbon at high temperatures reduces many metallic oxides to the respective metals.

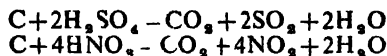


Sodium sulphate is reduced to sodium sulphide by heated carbon.

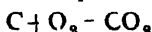


Hot concentrated sulphuric acid and nitric acid oxidise carbon to carbon dioxide. Hot sulphuric acid and nitric acid by the action of

carbon are reduced to sulphur dioxide and nitrogen dioxide respectively.



Experiment to prove that all the allotropic modifications of carbon consist of the same element If a certain fixed amount of each of the different allotropic modifications of carbon is separately burnt in pure and dry oxygen, the product is always carbon dioxide. Further, the same amount of any variety of carbon produces exactly the same weight of the gaseous product.



A porcelain boat containing a correctly weighed quantity of charcoal (sugar charcoal) is introduced in a hard glass tube one half of which is nearly packed with dry black cupric oxide from an open end. Through the one end of the tube nearer the boat, a slow stream of dry and pure oxygen is passed for some time. When the air inside the tube is displaced by oxygen, the other end is attached to a previously weighed potash bulb containing strong caustic potash solution. The layer of cupric oxide and the boat containing the charcoal are then strongly heated while a slow stream of oxygen is continually passed through the tube. The charcoal is burnt in oxygen producing carbon dioxide which is swept away by the oxygen gas and is absorbed in the potash bulb.

The increase in weight gives the weight of carbon dioxide formed. It has been found that 3.666 gms of carbon dioxide are produced when 1 gm of sugar charcoal is burnt.

If this experiment is performed with 1 gm of any other variety like graphite, diamond, animal charcoal etc., the same weight of the product (carbon dioxide) is obtained. It proves clearly that the different allotropic of carbon contain nothing but the same element carbon.

PHOSPHORUS

Symbol P	Atomic number 15
At wt 30.98	Electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^3$
Position in periodic table VB	

Phosphorus was discovered by the German alchemist Brand in 1674. The elementary nature of phosphorus was first established by Lavoisier in 1777.

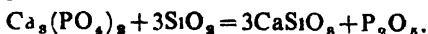
Phosphorus is so active that it cannot exist in nature in the free state. It was named phosphorus (phos - light phoro - I carry) for it glows in the darkness due to auto combustion. In the combined state it is widely distributed in various phosphatic minerals such as phosphorite $\text{Ca}_3(\text{PO}_4)_2$, fluorapatite $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$, chlorapatite $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$, vivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ etc. Animal bones contain about 60-80% $\text{Ca}_3(\text{PO}_4)_2$.

The phosphatic minerals (the most important of which is phosphorite, also called phosphate rock) and the bones are used as the source of phosphorus.

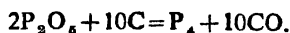
Preparation : Two methods are known for the manufacture of phosphorus.

(1) In the modern electrical process, phosphorus is made from either phosphate rock $\text{Ca}_3(\text{PO}_4)_2$ or bone ash. (2) In the old retort process, the element is extracted from the bone ash. At present, it has become advantageous to get phosphorus on a large scale by the electric process and the retort process is now obsolete.

(A) **Modern electro-thermal process :** The process is also called Parkar, Robinson, Readmann process according to the names of the discoverers. In this process, phosphorus is made by heating a mixture of powdered mineral calcium phosphate (or bone phosphate), sand and coke at a high temperature produced by means of an electric arc. Firstly at the high temperature of about 1200°C , calcium phosphate and silica react to produce calcium silicate and phosphorus pentoxide.



Phosphorus pentoxide is then reduced by coke to phosphorus at a still higher temperature of about 1500°C and carbon monoxide is produced.



The furnace made of fire-clay bricks is provided with two stout carbon electrodes near the bottom. Through these electrodes, an electric arc is struck so as to produce the high temperature.

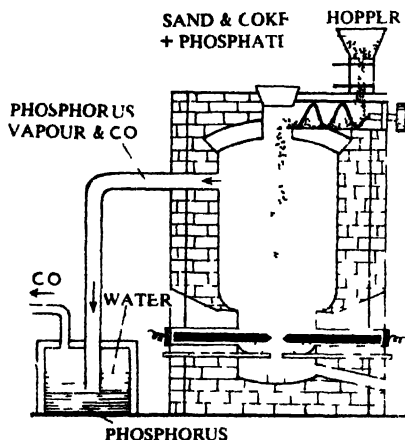


Fig. 2(38) Extraction of phosphorus by electrical process

The reacting mixture is introduced through the hopper at the top and is conveyed by means of a screw arrangement into the closed furnace bed. There is an outlet near the top of the furnace for the escape of phosphorus vapour and carbon monoxide. The calcium silicate formed is taken out through a small outlet at the bottom.

After introducing the charge through the hopper, the temperature of about 1500°C is generated by passing electric current through the electrodes.

Phosphorus liberated remains as vapours at this high temperature and the mixture of phosphorus vapour and carbon monoxide leaves the furnace through the outlet at the top. The mixture is then

bubbled through cold water under which phosphorus vapour condenses and collects there in the form of solid phosphorus. Carbon monoxide passes out as a gas.

The calcium silicate along with other impurities collects at the bottom as a liquid slag and is taken out at intervals.

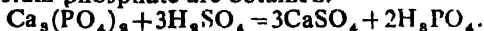
Phosphorus thus obtained is not pure. The crude phosphorus is melted under hot water to remove the sand and clay particles. It is then stirred with chromic acid ($K_2Cr_2O_7$ and conc. H_2SO_4) when some of the oxidisable impurities are oxidised and passed into the solution. Other impurities separate and rise up as a scum. The molten phosphorus under water is filtered by pressing through chamois leather or canvas and is finally cast into sticks.

Due to its spontaneous inflammability in contact with air, the pure phosphorus is always preserved under water and transported as such.

(B) The old retort process of manufacture from bones : Bones contain about 58% calcium phosphate, a little calcium carbonate, carbon, gelatin, fat and nitrogenous organic matter.

The bones are cut into small pieces and digested with carbon disulphide or carbon tetrachloride to remove fats and greasy substances. The pieces of degreased bones are then freed from gelatin by heating in super heated steam and is subjected to destructive distillation out of contact with air in an iron retort. The black mass that remains is the bone charcoal or bone black which is a mixture of carbon and calcium phosphate. Bone charcoal on being heated in air gives the bone ash containing 80% of calcium phosphate.

An intimate mixture of powdered bone ash and fairly strong sulphuric acid (60%) is heated when phosphoric acid and insoluble calcium phosphate are obtained.



Calcium sulphate is filtered off and the filtrate containing phosphoric acid is continually evaporated to a syrup. It is then mixed with powdered coke and carefully heated to complete dryness in cast iron vessels. The dried residue is next heated to redness in a fire clay retort, the mouth of which is dipped under water.

Phosphoric acid when heated decomposes first into metaphosphoric acid which is then reduced by charcoal to elementary phosphorus.



The reaction products, carbon monoxide and hydrogen, escape and phosphorus vapour condenses as a dark brown solid and collects under water.

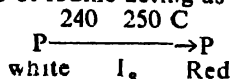
It has been stated before that the process is not used now.

Allotropic modifications of phosphorus : Phosphorus exhibits allotropy. It exists in several allotropic forms. Two important

allotropes are white or yellow phosphorus and red phosphorus. The latter is the stable form. Due to the difference in their molecular structures, the two forms show remarkable differences in their physical and in some chemical properties.

The phosphorus obtained by the modern electrical process or by old retort process is the white variety.

Preparation of red phosphorus from white phosphorus : Red phosphorus is prepared by heating white phosphorus at $240-250^{\circ}\text{C}$ in absence of air in an inert atmosphere of carbon dioxide or nitrogen with a trace of iodine acting as a catalyst.



White phosphorus with a trace of iodine is kept in a cast iron vessel fitted with an air tight cover through which passes an upright safety tube, open at both ends to prevent the increase of pressure inside the vessel. Two thermometers are placed in the two holes in the iron vessel. The vessel is carefully heated in a furnace to 240°C when white phosphorus is slowly converted into red phosphorus. A small portion of white phosphorus is oxidised to its oxides by the oxygen of the air initially present in the vessel.

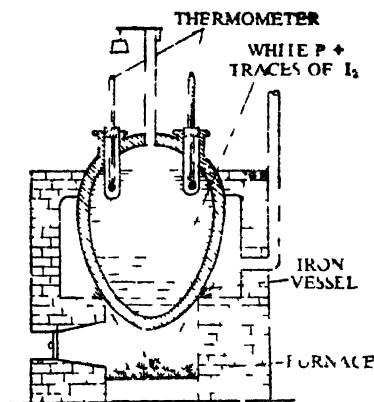


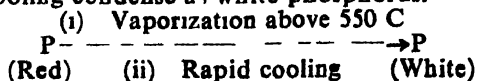
Fig 2.39) Preparation of red phosphorus

with hot water and dried by heating with steam.

Red phosphorus is not spontaneously oxidised in the air. Hence it is not kept under water.

When white phosphorus is kept in open air, it tends to transform slowly into the red phosphorus. Red phosphorus is also formed when white phosphorus is subjected to silent electric discharge.

Preparation of white phosphorus from red phosphorus : Red phosphorus is heated to above 550°C in an inert atmosphere of carbon dioxide or nitrogen when red phosphorus vaporizes. The vapours on cooling condense as white phosphorus.



Properties of white phosphorous : Physical :—(1) White phosphorus is translucent, almost colourless or pale yellow crystalline solid. It is soft, waxy and can easily be cut with a knife. (2) It has a garlic-like smell. (3) It melts at 44 C. (4) White phosphorus is heavier than water (sp. gr. 1.84). It is almost insoluble in water but soluble in organic solvents like carbon disulphide, alcohol, benzene, chloroform etc. (5) It is a non-conductor of heat and electricity. (6) It is a highly poisonous substance.

Chemical ; Phosphorus is a very active element. (1) Vapour density measurement shows that below 1000 C, the phosphorus molecule is tetratomic (P_4). The four P-atoms are situated at the four corners of a regular tetrahedron and are linked to one another by single covalent bonds [Fig. 2(39A)]. The P-P-P angle in the molecule is 60°. At about 1600 C, it is partially dissociated forming diatomic molecule. $P_4 \rightleftharpoons 2P_2$.

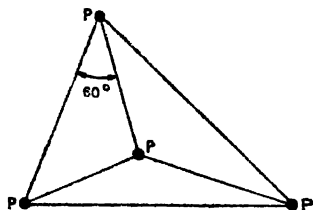


Fig. 2(39A)

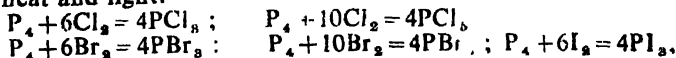
2) On heating, it is converted into red phosphorus. This conversion is almost complete when white phosphorus is heated at 250 C in an inert atmosphere of carbon dioxide or nitrogen.

(3) White phosphorus is easily oxidised to its various oxides by air or oxygen even at the ordinary temperature. When exposed to moist air, it undergoes spontaneous oxidation giving the lower oxide P_4O_6 along with a little ozone and emits a faint, green glow especially visible in the dark. This phenomenon is commonly known as *phosphorescence*. Even a trace of phosphorus is detected from the emission of this glow.

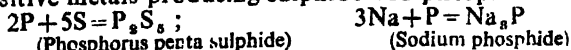
White phosphorus ignites in air even at 35 C producing the poisonous fumes of phosphorus pentoxide $P_4 + 5O_2 = 2P_2O_5$.

It has been found experimentally that the glowing of phosphorus increases if pressure of air is reduced. The emission of this light takes place in air containing traces of moisture. Many chemists are of opinion that the ozone formed during the spontaneous oxidation of phosphorus is responsible for phosphorescence to some extent.

(4) It ignites readily in halogens forming halides with evolution of heat and light.



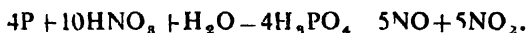
White phosphorus combines with sulphur and the highly electropositive metals producing sulphide and phosphides respectively.



(5) White phosphorus on being heated with a solution of caustic soda (or other strong alkalis like caustic potash, barium hydroxide etc) yields phosphine. Sodium hypophosphite is formed in solution.



(6) (a) White phosphorus acts as a reducing agent. It reduces hot, concentrated nitric acid to the oxides of nitrogen (such as nitric oxide, nitrogen dioxide) and it itself is oxidised to phosphoric acid



(b) White phosphorus precipitates copper, silver and gold from the aqueous solutions or their salts. When white phosphorus is added to a cold copper sulphate solution, copper is precipitated.



NB (i) Due to its spontaneous inflammability, white phosphorus is kept under water. Great care should be taken when using it, for it is very poisonous and catches fire easily.

(ii) If white phosphorus is accidentally dropped on the hand it should be removed immediately by washing with copper sulphate solution.

Experiments to illustrate some of the properties of white phosphorus

(1) **Cold flame** A few pieces of white phosphorus, covered with glass wools are taken in a round bottomed flask provided with

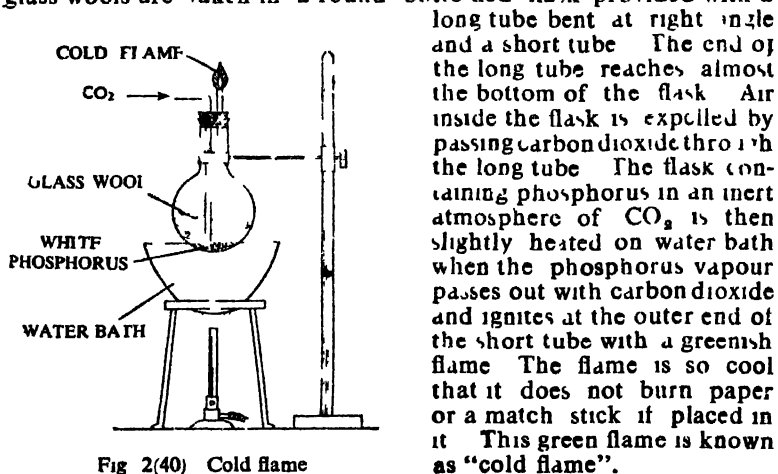


Fig 2(40) Cold flame

long tube bent at right angle and a short tube. The end of the long tube reaches almost the bottom of the flask. Air inside the flask is expelled by passing carbon dioxide through the long tube. The flask containing phosphorus in an inert atmosphere of CO_2 is then slightly heated on water bath when the phosphorus vapour passes out with carbon dioxide and ignites at the outer end of the short tube with a greenish flame. The flame is so cool that it does not burn paper or a match stick if placed in it. This green flame is known as "cold flame".

(2) **Cold fire** (a) A piece of white phosphorus is taken in a round bottomed flask containing water. A small quantity of potassium chlorate is kept near the piece of phosphorus. Now, conc. sulphuric acid is added on it carefully with the help of a thistle funnel. Phosphorus is found to burn under water emitting sparks.

(b) White phosphorus taken in a tube containing water is melted at 60°C . When air is blown through the tube, the melted phosphorus ignites under water.

Properties of red phosphorus

Physical (1) It is a red or reddish violet, odourless solid having a specific gravity of 2.2. (2) It has no definite melting point but becomes soft at 590°C . It vaporizes at above this temperature and the vapours produce white phosphorus by condensation. (3) It is insoluble in water and organic solvent like carbon disulphide. (4) It is a feeble conductor of electricity and is non-poisonous.

Chemical : Red phosphorus is much less reactive than white phosphorus. (1) It is not easily affected by air and shows no phosphorescence. When heated in air above 260°C , it produces phosphorus pentoxide. (2) It reacts with halogens slowly and burns in chlorine only when heated forming tri and penta chlorides. (3) Alkalis do not react with red phosphorus. (4) Conc. nitric acid is reduced to oxides of nitrogen by red phosphorus which is oxidised at the same time into phosphoric acid.

Comparison of the properties of white and red phosphorus

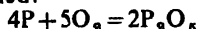
Property	White (yellow) phosphorus	Red phosphorus
Physical Colour, structure, smell, solubility and specific gravity	Almost colourless slightly yellowish with garlic smell. Soft but crystalline solid. Insoluble in water but soluble in carbon disulphide. It has the specific gravity of 1.8.	Opaque red solid, without any smell. Insoluble in water and CS_2 . Heavier than white phosphorus (specific gravity = 2.2).
Poisonous character and electrical conductivity	Very poisonous, non conductor of electricity.	Non poisonous and feeble conductor of electricity.
Melting and ignition points	It melts at 44°C , ignites in air at a low temperature (above 30°C).	Has no definite m.p. Ignites at high temperature (260°C), sublimates at 400°C .
Chemical reactivity.	Very reactive chemically. Less stable at ordinary temperature.	Less reactive than white phosphorus and stable at ordinary temperature.
Action of air — phosphorescence	Rapidly oxidises in air at ordinary temperature and shows green glow or phosphorescence, specially visible in the dark. It ignites in air even at 35°C producing P_2O_5 .	Not oxidised in air at ordinary temperature and shows no phosphorescence. Forms P_2O_5 when heated to 240°C in air.
Reaction with chlorine	Spontaneously ignites in chlorine giving phosphorus tri and penta chlorides.	Ignites in chlorine when heated yielding tri and penta chlorides.
Action of hot NaOH (or KOH) solution	Evolves phosphine and hypophosphite formed remains in solution.	Does not react.
Action of hot conc. nitric acid.	Reacts with explosion producing phosphoric acid and nitrogen dioxide.	Reacts comparatively slowly producing the same products as in the case of white phosphorus.

N.B. It is seen from the above comparative study that white phosphorus and red phosphorus differ remarkably in their physical as well as some chemical properties. The white variety is a soft, light, low-melting highly reactive substance while the red variety is hard, heavy, high-melting substance with less chemical reactivity. The differences between the two allotropes have been explained in the light of their molecular structures.

It has already been stated that the atomicity of phosphorus is 4. Investigations have revealed that the white phosphorus consists of individual P_4 molecules having very weak attraction between them. Moreover, the considerable strain existing in P_4 molecule with $P-P-P$ angles of 60° makes this allotrope highly reactive. On the other hand, the red phosphorus is made of tiny crystals in which tetrahedrally arranged P_4 units are joined through $P-P$ covalent bonds forming a long chain. This molecular structure is responsible for its chemical stability, high melting point etc.

Experiments to prove that white and red phosphorus consist of the same element :

(a) If equal masses of the two allotropes are heated in dry and pure oxygen, exactly the same masses of the product phosphorus pentoxide are obtained.



(b) x gms. of white phosphorus when heated with a trace of iodine to $250^\circ C$ in an inert atmosphere of nitrogen or carbon dioxide yield exactly x gms of red phosphorus and nothing else. On heating the same amount of red phosphorus at $550^\circ C$ in an inert atmosphere, the red variety is converted directly into vapour which on rapid cooling condenses to x gms of white phosphorus.

a trace of I_2
 x gms of white phosphorus $\xrightarrow{\text{in } CO_2 \text{ or } N_2, \text{ at } 250^\circ C}$ x gms of red phosphorus.

(1) vaporisation at $550^\circ C$ in CO_2
 $\xrightarrow{\hspace{10em}}$ x gms of white phosphorus.

(2) rapid cooling

These experimental evidences conclusively prove that the two allotropes are composed of the same element.

Uses : (1) White phosphorus is extensively used in the manufacture of red phosphorus. White phosphorus is used in the preparation of phosphorus pentoxide, phosphorus tri and pentachlorides, sodium, potassium and calcium hypophosphites, phosphor-bronze, (a rust-proof alloy of copper, tin and phosphorus). (2) It is used in making incendiary bombs, smoke screens and rat-poisons. (3) Red phosphorus is chiefly used in match industry. (4) In the laboratory preparation of hydrobromic and hydroiodic acids, red phosphorus is used.

N.B. The safety matches nowadays used is made of red phosphorus and oxidising agents. The match sticks are tipped with a paste of antimony sulphide, potassium chlorate (or potassium dichromate, red lead etc) and glue and dried. The two sides of the match boxes are pasted by a paper coated with red phosphorus, antimony sulphide, powdered glass or pure sand and gum. The friction of rubbing on the rough surface of the box with the stick generates enough heat to start the reaction between red phosphorus and the oxidising agent and sulphur of the antimony sulphide at the match-head burns. The wood is often impregnated with borax so that it does not continue to burn when it is blown out.

Comparison of the properties of nitrogen and phosphorus : Due to the similarities in chemical properties, nitrogen and phosphorus have been placed in the same group of elements in the periodic table.

Nitrogen (At. wt. 14.008)	Phosphorus (At. wt. 30.98)
(i) It is a non-metallic element occurring free in nature. At ordinary temperature, it is a gas and its molecules are diatomic (N_2).	(i) It is a non-metal. At ordinary temperature, it is a solid and it always occurs in the combined state in nature. At ordinary temperature, a molecule of phosphorus is tetratomic (P_4), white phosphorus is highly poisonous and shows phosphorescence.
It is non-poisonous and does not glow in the dark.	
(ii) Shows allotropy. It has only one allotropic modification called active nitrogen which is gaseous at ordinary temperature.	(ii) Shows allotropy. Familiar allotropes are white and red phosphorus. It has other allotropic modifications like violet, scarlet, and black phosphorus. All allotropes exist in the solid form.
(iii) Not very reactive chemically. It is neither combustible nor a supporter of combustion.	(iii) Very active chemically. White phosphorus catches fire even at the ordinary temperature and ignites in contact with chlorine etc.
(iv) Shows variable valency, ordinarily, tri and pentavalent in its compounds. Thus, nitrogen is trivalent in N_2O , NH_3 , NCl_3 etc. and pentavalent in NH_4Cl , NH_4Br , N_2O_5 etc.	(iv) It has more than one valency. Generally, tri and pentavalent in its compounds. Thus, it is trivalent in P_2O_3 , PCl_3 , PH_3 etc. and pentavalent in PH_4I , PH_4Cl , P_2O_5 , PCl_5 etc.
(v) Combines with oxygen at high temperature, $N_2 + O_2 \xrightarrow{3000^\circ C} 2NO$, Forms a number of oxides—	(v) White phosphorus ignites in air even at the low temperature of $35^\circ C$. $P_4 + 5O_2 \xrightarrow{35^\circ C} 2P_2O_5$
nitrous oxide (N_2O), nitric oxide (NO), nitrogen trioxide (N_2O_3), nitrogen tetroxide (N_2O_4), nitrogen pentoxide (N_2O_5). Some of the oxides are acidic oxides and react with cold water producing oxy-acids.	Forms several oxides— phosphorus trioxide (P_2O_3), phosphorus pentoxide (P_2O_5), phosphorus tetroxide (P_2O_4). P_2O_3 and P_2O_5 are acidic oxides producing acids with water. $P_2O_3 + 3H_2O \rightarrow 2H_3PO_3$ (in cold water). $P_2O_3 + H_2O \rightarrow 2HPO_3$ (in cold water). $P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$ (in hot water).
$N_2O_3 + H_2O = 2HNO_2$ (nitrous acid) $N_2O_5 + H_2O = 2HNO_3$	
(vi) Several hydrides of nitrogen are known. The main hydride, ammonia (NH_3) is colourless, pungent smelling gas soluble in water giving an alkaline solution.	(vi) Forms several hydrides. The main hydride is phosphine (PH_3) which is a colourless gas possessing an offensive smell like that of rotten fish. Almost insoluble in water. Shows slightly basic character in phosphonium compounds. $PH_3 + HI \rightarrow PH_4I$ (phosphonium iodide)
(vii) Combines with chlorine giving NCl_3 which is a very unstable, explosive liquid and undergoes hydrolysis in water $NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$. There is no compound having the formula NCl_4 .	(vii) Combines with chlorine giving comparatively stable compounds like PCl_3 , PCl_5 which undergo hydrolysis in contact with water. $PCl_3 + 3H_2O \rightarrow 3HCl + H_3PO_3$ $PCl_5 + 4H_2O \rightarrow 5HCl + H_4PO_4$
(viii) At high temperatures, it directly combines with metals like calcium, magnesium etc. producing the respective nitrides which suffer hydrolysis in hot water.	(viii) Combines with calcium, magnesium etc. forming phosphides at high temperatures. Metallic phosphides hydrolyse in hot aqueous solutions yielding phosphine.

Nitrogen (At. wt. 14.008)

$\text{Ca}_3\text{N}_2 + 6\text{H}_2\text{O} = 3\text{Ca}(\text{OH})_2 + 2\text{NH}_3$
 (ix) Does not react with chlorine, iodine directly. Sulphur, alkalis, strong and hot nitric acid have no action on nitrogen.

Phosphorus (At. wt. 30.98)

$6\text{Ca} + \text{P}_4 = 2\text{Ca}_3\text{P}_2$
 $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} = 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$
 (ix) Ignites in contact with iodine producing PI_3 . Sulphur gives different sulphides under different conditions. Alkalis, strong and hot nitric acid react with phosphorus giving phosphine and phosphoric acid respectively.

SULPHUR

Symbol S

Atomic number 16

At. wt. 32.06

Electronic configuration

Position in the periodic table VI B

 $1s^2 2s^2 2p^6 3s^2 3p^4$

That sulphur is a distinct element was first recognised by Lavoisier in 1774. Its existence in the free state and some of its characteristic properties were known to the ancients.

The uses of sulphur in medicines and in industries was known in our country even in the period of the Hindu civilisation.

Sulphur is widely distributed in nature in the free state. In combination with metals, it also occurs in nature as various sulphides and sulphates.

Extraction of sulphur : Sulphur is extracted and purified from the sulphur bearing rocks present in nature. Deposits of free sulphur occur in abundance in the volcanic regions of Sicily and Japan. Nowadays, the sulphur deposits in Louisiana and Texas in America are considered to be the main source of sulphur. About 80 per cent of the total sulphur consumed in the world is obtained from the American source.

Two methods are generally employed for extraction of sulphur from its deposits. These are : (a) *Sicilian process*—used for working up the Italian deposits. (b) *American or Frasch process*—used for raising sulphur in U. S. A.

(A) Sicilian Process : Sulphur bearing rocks found in Sicily contain about 20—25% free sulphur besides other impurities such as clay, sand, limestone, gypsum etc. In this process, sulphur is separated from the said impurities by the process of *liquation*. The rocks are stacked with air spaces on the sloping floor of brick-made sulphur-kilns (also called *calcaroni*) situated on the sloping hill sides and ignited at the top. About $\frac{1}{3}$ rd of sulphur is burnt and escapes in the form of sulphur dioxide. But this reaction is highly exothermic and the heat of reaction melts the remaining portion of sulphur which flows down the sloping floor of the kilns and collects in the wooden vats. The crude sulphur thus obtained contains about 5% rocky impurities. In this process, a considerable portion of sulphur is used as fuel and is lost. Since fuels like coal, woods etc. are very costly in Sicily, it is cheaper to use native sulphur as fuel than the imported coal.

The process of extraction of sulphur from Sicilian deposits has been improved by using Gill regenerative kiln which consists of 4 brick-chambers connected with one another and arranged in circle. The hot gases from one chamber in which sulphur has melted are made to pass into the adjoining chamber to heat up the crude sulphur there. Thus, the process continues in series and the fuel expense is minimised.

Crude Sicilian sulphur is purified by distillation at Marseilles in France where the fuel is much cheaper.

Purification of sulphur : The impure sulphur is melted in an iron pot and the molten sulphur drains by means of a pipe into a cast iron retort heated over a fire. Sulphur boils and the vapour is led into a large brick-work chamber where it condenses first on the cold walls as a light yellow powder called *flowers of sulphur*. As the process of distillation continues, the walls of the chamber become hot and when the temperature rises above 113°C , the pure distilled sulphur melts into a liquid and collects upon the floor. The liquid is then cast into cylindrical rods by tapping through the hole and is sold as *roll-sulphur*.

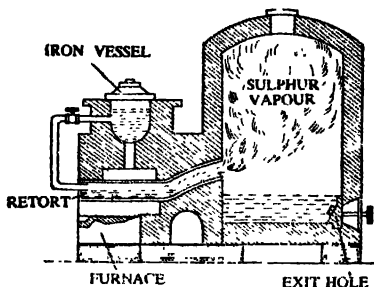


Fig. 2(41) Purification of sulphur.

To get the purest form of sulphur, the roll-sulphur is dissolved in carbon disulphide, filtered and the filtrate is evaporated to dryness. The residue left is the pure rhombic sulphur.

(B) American or Frasch process : The deposits in which sulphur occurs in Louisiana and Texas are peculiar in character. The free sulphur bed lies below the layers of clay, sand and limestone at a depth of about 800 feet from the earth's surface. The process of extraction of American sulphur was invented by Frasch and consists of passing superheated water under pressure into the sulphur bed, melting the sulphur and forcing it through a tube to the surface. In this process, three concentric pipes are introduced into the sulphur deposit through a hole bored down through the clay, sand and lime stone. Water heated to 170°C under a pressure of 10-18 atms. is sent down through the outermost of the three pipes (No 1 in the fig.). This super heated water melts the sulphur below and the molten sulphur flows into the reservoir at the base of the hole.

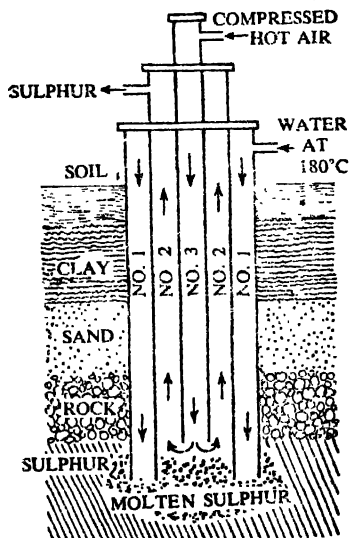


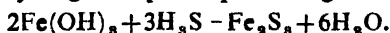
Fig. 2(42) Extraction of sulphur by American process

A blast of hot compressed air at a pressure of about 35 atms.

is then passed in through the innermost pipe (No 3 in the fig), when a frothy emulsion of molten sulphur, water and air bubbles rises up the surface through the middle pipe (No 2 in the fig). This sulphur is then collected in the wooden vats. It solidifies on cooling and is separated from water. Sulphur thus obtained is of 99.5%–99.9% purity.

Extraction of sulphur from other sources : Sulphur may be chemically recovered from different sulphur compounds produced during various industrial and metallurgical operations.

(a) *From spent oxide of iron of gas works :* Some hydrogen sulphide remains as impurity in the coal gas obtained by destructive distillation of coal containing iron pyrites (FeS_2). To absorb hydrogen sulphide, coal gas is passed through the purifiers containing hydrated oxide of iron (ferric hydroxide). Ferric oxide (hydrated) reacts with hydrogen sulphide producing ferric sulphide.

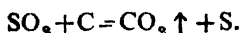


When the oxide is completely converted into the sulphide, it loses its power of absorbing H_2S and is called the spent oxide. The spent oxide is kept exposed to the air where the hydrated ferric oxide is regenerated with the separation of sulphur. The separated sulphur is then collected.



(b) *From calcium sulphide. a by-product of Leblanc alkali manufacturing process :* Sulphur may also be obtained from calcium sulphide obtained as the by-product in the manufacture of sodium carbonate by Leblanc process. Since this process of alkali manufacture is now obsolete, this process of recovering sulphur is no longer in use.

(c) *From sulphide ores* Large quantities of sulphur dioxide obtained as a by-product in the extraction of copper, lead and zinc from their sulphide ores are absorbed in a cold solution of sodium sulphite containing aluminium sulphate. The solution on being heated evolves sulphur dioxide which is then passed over white hot coke (1100 C). Sulphur dioxide is reduced to sulphur. Sulphur obtained by reduction volatilises and is condensed on cooling.



(d) *From gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$:* Gypsum when heated to about 1400 C with sand, clay and coke produces sulphur dioxide. Sulphur can be obtained from SO_2 by the method discussed above.

Allotropic modifications of sulphur : Sulphur exists in several allotropic modifications. The allotropes do not differ much chemically but show considerable differences in their physical properties. Of the five important allotropic forms—two are crystalline and three amorphous.

Crystalline allotropes : (1) **Rhombic or octahedral or α -sulphur :** When roll sulphur is dissolved in carbon disulphide and the solution is slowly evaporated, transparent lemon-yellow octahedral

crystals of sulphur are obtained. The naturally-occurring sulphur remains in the rhombic or α -form. It is the most stable form at the ordinary temperature. All other allotropes are slowly converted into the rhombic sulphur on keeping. Its density is 2.05. It melts at 113°C . It is insoluble in water but soluble in carbondisulphide, hot chloroform, benzene etc. It is a non conductor of heat and electricity. Its formula in the vaporous state and in solution is S_8 .

(2) **Monoclinic or prismatic or β -sulphur** : At about 96.5°C , rhombic sulphur is converted into the monoclinic form.

This variety is easily obtained by melting rhombic sulphur in a porcelain crucible and cooling it slowly until a solid crust is formed on the surface. Now, the crust is pierced at two points with needles and still liquid portion of sulphur is poured off. On removing the crust, long needle-shaped transparent yellow crystals of monoclinic sulphur are found in the crucible.

It is a brittle, transparent and amber-yellow crystalline solid. Its density is 1.93. It melts at 120°C . It is insoluble in water but dissolves readily in carbon disulphide. It is unstable at ordinary temperature and tends to pass into the rhombic variety on standing. It is to be noted that rhombic sulphur is stable below 96.5°C and the monoclinic sulphur is stable above 96.5°C . So, 96.5°C is the transition temperature at which both the varieties are stable and remain in equilibrium.



Thus, the rhombic form can be converted into the monoclinic form and vice versa by a rise or fall of temperature.

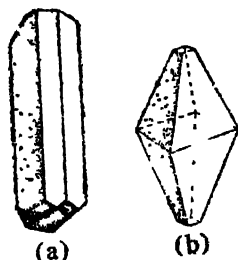
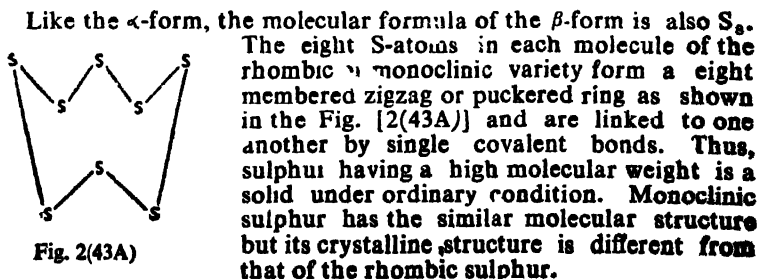
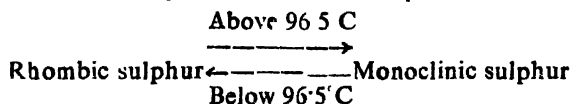


Fig. 2(43) Crystals of sulphur
(a) Prismatic (b) Rhombic

Amorphous sulphur : (1) Plastic or γ -sulphur : Powdered roll sulphur is melted to a mobile liquid by heating in a test tube. The melted sulphur on being heated further nearly to its boiling point is converted into a dark brown liquid which is then poured in thin stream in cold water in a beaker. It solidifies to a soft rubber like elastic material called plastic sulphur.

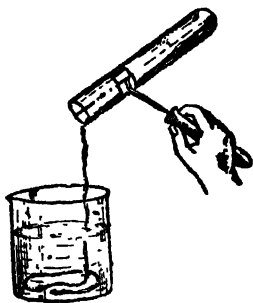


Fig. 2(44) Plastic sulphur into the stable rhombic form on standing.

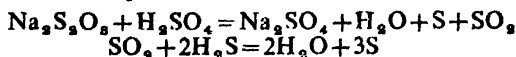
Plastic sulphur is an elastic amber-coloured solid which can be drawn into flexible threads or can be given any desired shape. Its sp. gr. is 1.95. It is insoluble in water and carbon disulphide. At ordinary temperature, it hardens slowly and passes

(2) Milk of sulphur or δ -sulphur : It is obtained by treating a polysulphide like CaS_8 or yellow ammonium sulphide with dilute hydrochloric acid.

The red solution obtained by heating powdered roll sulphur with milk of lime is filtered. The filtrate is treated with a little hydrochloric acid when milk of sulphur is precipitated out.

It is an amorphous variety of sulphur. Its sp. gr. is 1.82. It is insoluble in water but highly soluble in carbon disulphide. It is used in medicine.

(3) Colloidal sulphur : A milky suspension of colloidal sulphur is obtained by adding dilute mineral acids on sodium thiosulphate or by passing sulphuretted hydrogen through a solution of sulphur dioxide. Colloidal sulphur may also be obtained by pouring an alcoholic solution of roll sulphur into an excess of cold water. It is soluble in carbon disulphide and is used in medicine.



Properties of sulphur : Physical—(1) Ordinary sulphur is a pale yellow, crystalline, solid non-metal. (2) It is brittle and non-conductor of heat and electricity. (3) It shows allotropy. The different allotropes have different melting points. Rhombic sulphur melts at 113°C giving a yellow mobile liquid, the colour of which deepens with rise of temperature. The action of heat on sulphur is interesting and is stated below.

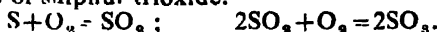
Action of heat on sulphur : Liquid sulphur undergoes remarkable changes in colour, mobility, viscosity etc. when it is heated gradually. Sulphur melts to a clear yellow mobile liquid at $118^\circ\text{--}119^\circ\text{C}$ which darkens in colour and turns to deep orange with rise of temperature. At temperatures between $160^\circ\text{--}180^\circ\text{C}$, the liquid loses its mobility and becomes viscous. The liquid is almost black and more viscous at 230°C . Beyond 230°C , the mobility is however regained. At 444.6°C , liquid

sulphur begins to boil. Reverse changes occur when the boiling sulphur is allowed to cool down slowly.

The change in viscosity above 160°C is due to the fact that the molten sulphur contains two allotropes S_{λ} (soluble in CS_2) and S_{μ} (insoluble in CS_2) in equilibrium; $S_{\lambda} \rightleftharpoons S_{\mu}$. The percentage of S_{μ} suddenly increases when heated above 160°C . As a result, the molten sulphur becomes viscous more and more.

(4) Sulphur is insoluble in water but soluble in carbon disulphide and other organic solvents like hot benzene, turpentine etc. Plastic sulphur is insoluble in carbon disulphide.

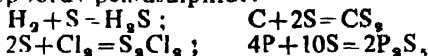
Chemical: Sulphur is a chemically active element. (1) It is an easily combustible substance. When heated in oxygen or air, it melts and burns with a pale blue flame forming sulphur dioxide with a trace of sulphur trioxide.



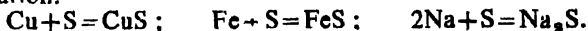
Ignition of a mixture of sulphur and potassium nitrate or potassium chlorate leads to deflagration or explosion.

(2) Sulphur combines directly with many non-metals and metals either at room temperature or when heated producing the corresponding sulphides.

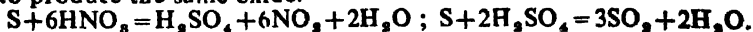
When sulphur vapour and hydrogen are passed over red hot pumice stone, gaseous hydrogen sulphide is obtained. As a result of the reaction between boiling sulphur and chlorine, sulphur mono chloride, an orange liquid, is produced. Red hot carbon reacts with sulphur vapours yielding carbon disulphide which is a liquid at the ordinary temperature. It readily combines with phosphorus to give phosphorus pentasulphide.



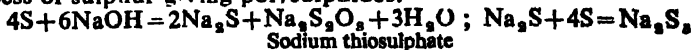
When heated, sulphur combines with metals like copper, zinc, mercury, iron, sodium etc. forming the metallic sulphides. A very thin strip of copper burns brilliantly with a yellow flame in sulphur vapour. Sodium or potassium catches fire in sulphur vapour with deflagration.



(3) It is not acted upon by dil. mineral acids and conc. hydrochloric acid. When boiled with conc. nitric or sulphuric acid, sulphur is oxidised. Conc. nitric acid (with bromine as the catalyst) oxidises sulphur to sulphuric acid and itself is reduced to nitrogen dioxide; sulphur is oxidised by hot concentrated sulphuric acid to sulphur dioxide. In this reaction, the acid is also reduced to produce the same oxide.



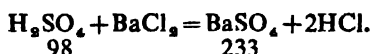
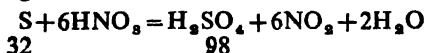
(4) Sulphur dissolves in hot alkalis leading to the formation of sulphides and thiosulphates. The sulphides may combine with excess of sulphur giving polysulphides.



Thiosulphate radical ' S_2O_3 ' is formed when an atom of oxygen of the sulphate radical ' SO_4 ' is replaced by a sulphur atom.

Experiment to prove that all allotropic modifications of sulphur consist of the same element : If a certain fixed quantity of each of the different allotropic modifications of sulphur is separately burnt in pure and dry oxygen, equal weight of the same product sulphur dioxide is obtained. $S + O_2 = SO_2$.

1 gm. of pure powdered rhombic sulphur taken in a small beaker is mixed with fuming nitric acid and the beaker is then heated on a sand bath. Sulphur dissolves completely and is oxidised producing sulphuric acid. The solution when cold is diluted with excess of distilled water and boiled again. To the warm solution, a solution of barium chloride is added till barium sulphate is completely precipitated. The precipitated barium sulphate is collected by filtration, washed several times with distilled water and dried in a desiccator. The weight of the perfectly dried sulphate is found to be 7.28 gms.



It is evident from the equations that 32 gms of sulphur give 233 gms of barium sulphate i.e. 1 gm of sulphur produces 7.28 gms of $BaSO_4$.

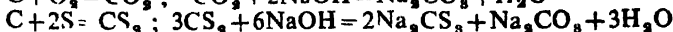
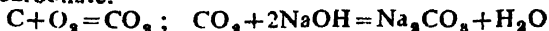
The same experiment is repeated with 1 gm of each of the other varieties of sulphur. It is found that in all the cases, the weight of barium sulphate formed is exactly 7.28 gms. Thus, it is experimentally established that the different allotropes of sulphur contain nothing but the same element sulphur.

Uses : (1) The most important use of sulphur is in the large scale preparation of sulphuric acid. (2) It is used in the manufacture of gun powder and for the vulcanization of rubber, a process which converts the soft pliable rubber into the hard, tough substance of which motor tyres and similar products are made.

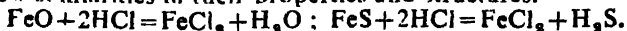
(3) Refined sulphur finds application in medicine as an ointment for the treatment of skin diseases. (4) Sometimes, it is used as a disinfectant, as a fungicide in agriculture and as an insulator. (5) Large quantities of sulphur are used in making calcium bisulphite which is used as a bleacher of wood pulp in the paper industry. It is largely used in the preparation of other important sulphur compounds such as carbon disulphide, sulphur chloride (solvent), phosphorus penta sulphide (used in match-sticks), sodium thiosulphate (used in photography), vermilion and ultramarine (used as pigments).

Comparison between sulphur and oxygen : Due to their chemical resemblances, sulphur and oxygen are regarded as the members of the same family of elements and have been placed in same group (group VIB) in the periodic table.

Similarities : (1) Both the elements are found to occur free in nature. (2) Both of them exhibit allotropy. Ozone is the allotropic modification of oxygen. Sulphur exists in both crystalline and amorphous allotropic forms. (3) Both sulphur and oxygen unite chemically with hydrogen yielding more than one compound such as H_2O , H_2O_2 , H_2S , H_2S_2 , etc. (4) Carbon burns in oxygen giving carbon dioxide (acidic oxide) which reacts with alkalis to produce carbonates. Red hot carbon and sulphur vapour combine chemically producing carbon disulphide which reacts with alkalis to give thio carbonate.



(5) Both combine with the metals ; oxygen forms metallic oxides and sulphur gives sulphides. These oxides and sulphides show similarities in their properties and structures.



Dissimilarities : (1) At the ordinary temperature, oxygen is a colourless gas while sulphur is a slightly yellow solid. (2) Oxygen shows a fixed valency of 2 in almost all its compounds but sulphur exhibits variable valency in different compounds. (3) An oxygen molecule is diatomic and the two atoms are covalently linked to form the molecule. In oxygen, the attraction between its individual molecules is feeble and this is why oxygen is a gas. But the atomicity of sulphur depends on the temperature. Ordinarily, its molecule consists of eight atoms which are linked covalently forming a puckered octahedral ring. Due to this structure with a high molecular weight, sulphur is a solid under ordinary condition. (4) Oxygen is not inflammable but is a supporter of combustion but sulphur is an easily combustible substance. (5) The main compound of oxygen and hydrogen is water (H_2O) which is a neutral liquid. But the corresponding compound of sulphur and hydrogen is hydrogen sulphide (H_2S) which is a weak acid. (6) The oxide of chlorine, Cl_2O is an explosive but the corresponding compound of sulphur with chlorine is not an explosive.

THE HALOGENS

The four non-metals fluorine, chlorine, bromine and iodine form a family of closely allied elements known as the halogens, meaning, literally, sea-salt producers (Greek, *halo* = sea salt and *genes* = produce), as these elements react with most metals to form compounds similar to the sea-salt, sodium chloride. The binary compounds of these elements with other elements are called the halides.

Of the four elements, chlorine was first isolated from NaCl. The presence of bromides and iodides in sea water was detected at a later stage. The chemistry of fluorine is not discussed here as the element has not been included in the syllabus.

✓ CHLORINE

Symbol Cl
Molecular formula Cl_2
Atomic weight 35.456

Atomic number 17
Electronic configuration
 $1s^2 2s^2 2p^6 3s^2 3p^5$
Position in periodic table VII B

Chlorine was discovered and first isolated by Scheele in 1774. The elementary nature of the gas was conclusively proved in 1810 by Davy who called it chlorine on account of its colour (Greek *chloros* = greenish yellow.)

Being very reactive chlorine does not occur free in nature but exists in large quantities as chlorides of many metals. The most important source of chlorine is the common salt or the rock salt, NaCl . Sea water contains about 2–3 percent of sodium chloride. Besides, it occurs abundantly in minerals like *sylvine* (KCl) and *carnallite* ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) in the Stassfurt deposits in Germany.

Preparation : (A) By oxidising concentrated hydrochloric acid .

(a) **Laboratory method :** In the laboratory, chlorine is prepared by heating concentrated hydrochloric acid with powdered manganese dioxide. Manganese dioxide acts as an oxidising agent and oxidises hydrochloric acid into chlorine.



Some powdered manganese dioxide is taken in a round bottomed flask fitted with a thistle funnel and a delivery tube. Concentrated hydrochloric acid is poured down the funnel so that manganese dioxide and the end of the thistle funnel remain well under the acid. A deep brown solution is formed in the flask. The mixture is then slightly warmed. Greenish yellow chlorine gas together with certain amount of hydrogen chloride and water vapour is evolved. The gas coming out of the delivery tube is then passed successively through two wash bottles, the first one containing water and the second conc. sulphuric acid. Water dissolves hydrogen chloride and the concentrated sulphuric acid removes moisture.

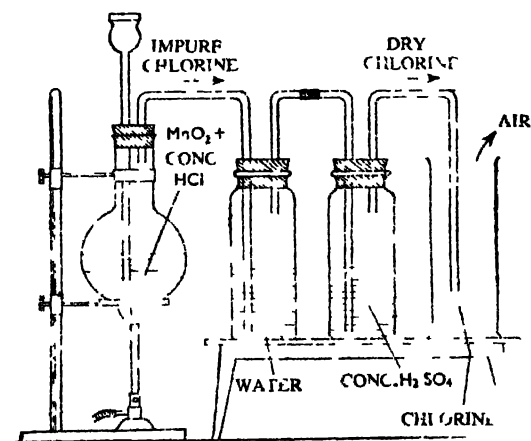


Fig. 2(45) Preparation of chlorine in the laboratory.

Chlorine thus dried and purified is collected in dry gas jars by upward displacement of air.

N.B. (i) When chlorine is bubbled through water, water absorbs the acid vapour together with some chlorine gas. But the water soon becomes saturated in respect of chlorine which then passes on ; HCl being much more soluble continues to be absorbed in water which still remains unsaturated with respect to hydrogen

chloride. Chlorine can be collected by the downward displacement of saturated brine or hot water in which the gas is much less soluble. It is not collected over cold water for its solubility or over mercury which is attacked by gaseous chlorine.

(ii) The reaction between MnO_2 and conc. HCl takes place in two stages. The dark brown solution formed in the cold contains manganese trichloride which decomposes on warming with liberation of chlorine and formation of manganous chloride in solution.

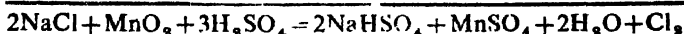
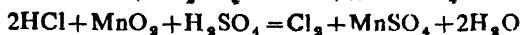
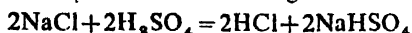


Or,



(b) From a chloride, conc. H_2SO_4 and MnO_2 :

Chlorine can be prepared by heating a mixture of manganese dioxide, 50% sulphuric acid and a chloride (like NaCl , KCl etc). The reaction proceeds in two stages :

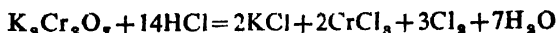


Conc. H_2SO_4 first acts upon sodium chloride to form hydrogen chloride which is then oxidised to chlorine by manganese dioxide.

The apparatus, purification and collection are the same as described under the laboratory method. Bromine and iodine can also be prepared from a bromide and an iodide respectively by applying this process. So this method is regarded as a general method of preparation of these elements.



(c) Hydrochloric acid can be oxidised to chlorine by other oxidising agents. Potassium dichromate and lead dioxide oxidise hydrochloric acid under hot condition.



The oxidation of HCl can be brought about by potassium permanganate at the ordinary temperature.

Preparation of pure chlorine at the ordinary temperature : When concentrated hydrochloric acid and crystals of potassium permanganate are made to interact at the room temperature, hydrochloric acid is oxidised to produce chlorine. This is a convenient method of getting regulated supply of chlorine in the laboratory.



Crystals of potassium permanganate are taken in a conical flask

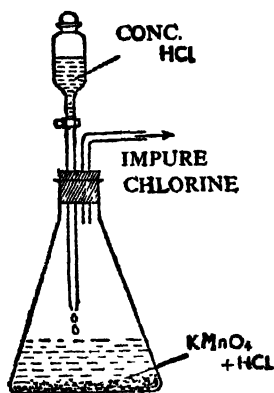


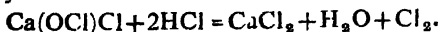
Fig. 2(46) Preparation of chlorine at ordinary temp.

fitted with a dropping funnel and a delivery tube. Cold and concentrated hydrochloric acid is then dropped cautiously on the crystals from the dropping funnel. The reaction starts as soon as the permanganate and the acid come in contact with each other. Chlorine begins to evolve and is collected by the upward displacement of air.

The reaction becomes vigorous and may take place with explosion if excess of hydrochloric acid is added rapidly.

Chlorine may be prepared in a Kipp's apparatus when a steady supply of the gas is required for occasional use. In this case, solid potassium permanganate is to be taken in the central globe of the apparatus and concentrated hydrochloric acid is to be added through the funnel attached to the upper globe.

(d) Chlorine is also obtained at the ordinary temperature by the action of bleaching powder on dilute hydrochloric acid.



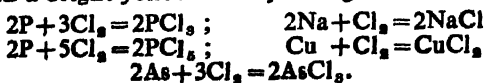
(B) **Electrolysis of hydrochloric acid or some fused chlorides :** When a strong aqueous solution of hydrochloric acid or fused sodium chloride, tin chloride or silver chloride is electrolysed, chlorine is liberated at the anode.

Very pure chlorine is obtained by electrolysing fused silver chloride in a hard glass U-tube fitted with carbon electrodes.

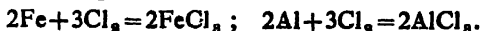
Properties : Physical—(1) Chlorine is a greenish yellow gas with a choking, unpleasant, irritating smell. (2) It is very poisonous. (3) It is 2.5 times heavier than air. (4) It is moderately soluble in water but is very slightly soluble in brine or hot water. It is much less soluble than hydrochloric acid and may be freed from traces of the latter by passing it through water. (5) It can be easily liquefied by compressing the cooled gas.

Chemical : Chlorine is a very reactive element.

(I) *Chlorine is not inflammable but supports combustion of many non-metals and metals.* Finely powdered arsenic, antimony, pieces of white phosphorus, thin copper foils etc. catch fire spontaneously when sprinkled into a jar of chlorine with the formation of the respective chlorides of the elements. Sodium burns in chlorine with a bright yellow flame yielding sodium chloride.

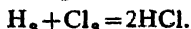


Iron, zinc, aluminium etc. directly unite with chlorine at elevated temperatures forming their chlorides.

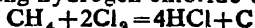


Although chlorine combines directly with most elements, it has no action upon carbon, nitrogen. So the chlorides of these elements are prepared by the application of indirect methods.

(2) *Chlorine has got great affinity for hydrogen.* Chlorine does not react with hydrogen in the dark but a mixture of chlorine and hydrogen when exposed to sunlight explodes violently forming hydrogen chloride. A burning jet of hydrogen continues to burn in a jar of chlorine with the production of fumes of hydrogen chloride.



Chlorine not only reacts with free hydrogen but also with hydrogen present in other compounds. Thus, when exposed to direct sunlight or heated, a mixture of methane and chlorine reacts with explosion yielding hydrogen chloride and setting free carbon.



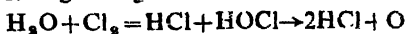
A piece of filter paper soaked in turpentine ($\text{C}_{10}\text{H}_{16}$) takes fire immediately when plunged into chlorine. Carbon is set free in the form of soot.

Due to great affinity for hydrogen, chlorine behaves as a strong oxidising agent.

(3) *The reaction between chlorine and water depends on the conditions of temperature and light.*

(a) When chlorine is passed into ice-cold water (0°C), crystals of different hydrates ($\text{Cl}_2 \cdot 10\text{H}_2\text{O}$, $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$, $\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ etc.) are obtained.

(b) Chlorine dissolves fairly in water at the ordinary temperature giving a light yellow solution known as chlorine water. This solution smells strongly of chlorine. It is probable that chlorine water contains hydrochloric acid and hypochlorous acid. On standing for a long time, hypochlorous acid decomposes to produce nascent oxygen. The formation of nascent oxygen is facilitated by strong sunlight.



(c) In bright sunlight, chlorine decomposes water giving hydrochloric acid and oxygen. This reaction is reversible.



(4) *Chlorine is a strong electro negative element and a powerful oxidising agent.* It oxidises many substances by uniting with them

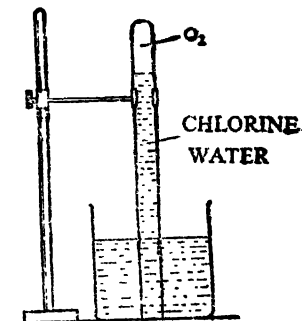
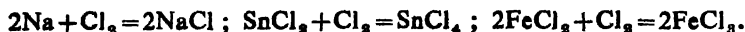
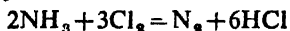


Fig. 2(47) Reaction of chlorine and water in bright sunlight

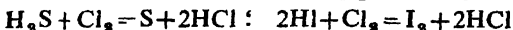
directly. Thus, chlorine oxidises metallic sodium to sodium chloride, stannous chloride to stannic chloride, a greenish or almost colourless solution of ferrous chloride to a yellow solution of ferric chloride.



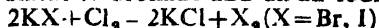
Chlorine can also oxidise by removing hydrogen or an electropositive element from a substance. Gaseous chlorine oxidises ammonia to nitrogen (nitrogen trichloride, a violently explosive liquid, is formed if chlorine is in excess). When chlorine is introduced into a jar of hydrogen sulphide, yellow sulphur is set free or chlorine precipitates sulphur from an aqueous solution of hydrogen sulphide. Hydroiodic acid, on being reacted with chlorine, is oxidised to iodine. In all the above reactions, chlorine itself is reduced to hydrochloric acid.



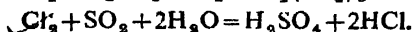
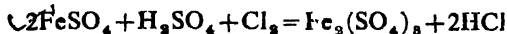
(HCl formed reacts with excess of NH_3 producing NH_4Cl)



It oxidises a bromide to bromine and an iodide to iodine.



Chlorine oxidises acidified ferrous sulphate solution to ferric sulphate and an aqueous solution of sulphur dioxide (sulphurous acid) to sulphuric acid. As usual, chlorine is reduced to hydrochloric acid. In each of the above two cases, chlorine exhibits its oxidising action in presence of an acid or water by actually adding oxygen to a substance.

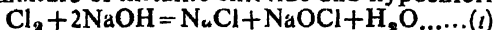


Chlorine possesses strong bleaching properties. Chlorine bleaches by oxidation. Dry chlorine has no bleaching action. Chlorine can bleach vegetable colours in presence of moisture. Actually, the nascent oxygen liberated by the reaction between chlorine and moisture is responsible for bleaching vegetable colouring matter.

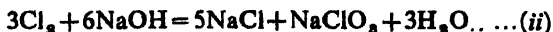


Vegetable colouring matter + O → oxidised, colourless product

(5) *Chlorine acts on alkalis giving different products under different conditions.* When chlorine is passed into a dilute solution of alkali (e.g. caustic soda or caustic potash) so that excess of alkali remains, a mixture of metallic chloride and hypochlorite is formed.

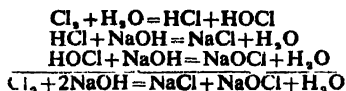


When excess of chlorine is passed into a hot and concentrated solution of an alkali, we get a mixture of metallic chloride and chlorate.

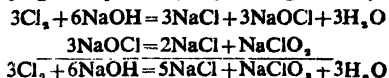


Here, the hypochlorite formed in the cold is decomposed into chloride and chlorate under hot condition.

It is to be remembered that the reaction represented by the equation (i) takes place in stages as described below.

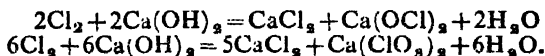


Again on multiplying the equation (i) by 3, we get the equation (ii).

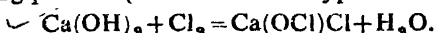


Chlorine will react with caustic potash giving similar products.

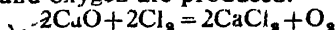
Chlorine reacts with cold and excess of lime water or dilute aqueous solution of calcium hydroxide producing calcium chloride and calcium hypochlorite. But hot milk of lime on being treated with excess of chlorine yields a mixture of calcium chloride and calcium chlorate.



Dry chlorine gas, when passed over dry slaked lime at 40°C gives bleaching powder (calcium chloro hypochlorite).

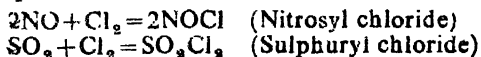


Chlorine does not react with calcium oxide at the ordinary temperature. When chlorine reacts with calcium oxide at a red heat, calcium chloride and oxygen are produced.



(b) Chlorine combines directly with many non-metallic oxides producing *additive compounds*. Carbon monoxide and chlorine react together to form a poisonous additive compound known as carbonyl chloride. The compound is also known as phosgene.

$\text{CO} + \text{Cl}_2 = \text{COCl}_2$. Nitric oxide and sulphur dioxide give similar additive compounds with chlorine.



Unsaturated organic substances like ethylene, acetylene etc. also react with chlorine yielding additive compounds.



Experiments to illustrate the important properties of chlorine :

(1) Chlorine does not burn but is a supporter of combustion of many non-metals and metals. (a) When a piece of dry white phosphorus taken on a deflagrating spoon is introduced into a jar of chlorine, phosphorus ignites spontaneously forming phosphorus tri and penta chlorides.



(b) Finely powdered arsenic or antimony catches fire immediately when sprinkled into a gas-jar of chlorine. As a result, arsenic or antimony chloride is formed.

(c) When a piece of molten sodium taken on a deflagrating spoon is lowered into a jar of chlorine, the metal burns with a bright yellow flame.

(d) If thin leaves of copper foils are inserted in a jar of chlorine, the metal burns in the gas spontaneously with a green flame.

(2) *Chlorine has strong affinity for hydrogen.*

(a) A test tube is filled up with a mixture of equal volumes of hydrogen and chlorine and is wrapped with a towel. When the mouth of the test tube is held before a flame, the gases unite instantaneously with a sharp explosion and fumes of hydrogen chloride are given off. $\text{Cl}_2 + \text{H}_2 = 2\text{HCl}$.

When a burning jet of hydrogen is introduced into a gas-jar full of chlorine, the hydrogen continues to burn with a greenish flame and clouds of fumes of hydrogen chloride are seen, whilst the greenish yellow colour of chlorine gradually disappears.

(b) If a lighted candle is lowered into a gas-jar filled with chlorine, the candle burns in the gas with a dull-red smoky flame with the formation of hydrogen chloride and liberation of free carbon in the form of soot. In this case, chlorine attacks the hydrogen of paraffin of which the candle is composed of leaving the black carbon behind. This experiment proves conclusively that chlorine is without action upon carbon.

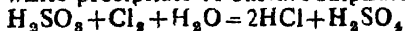
(3) *Chlorine decomposes water at bright sunlight evolving oxygen :*
A long glass tube closed at one end is filled completely with chlorine water and kept inverted over water.

When the tube is exposed to bright sunlight, chlorine water gets decomposed with the evolution of bubbles of oxygen which is collected at the upper part of the tube. That the evolved gas is oxygen is proved by the fact that it immediately rekindles a glowing chip of wood.

(4) *Chlorine is an oxidising agent :*

(i) When chlorine is passed through a solution of ferrous chloride, ferric chloride is formed and the solution becomes yellow in colour. On adding a few drops of potassium ferrocyanide solution to it, a blue precipitate is obtained. This confirms the presence of ferric ions (Fe^{+3}) in the solution.

(ii) When chlorine is passed through a solution of sulphur dioxide in water (sulphurous acid), the latter is oxidised to sulphuric acid which on being treated with barium chloride solution gives a white precipitate of barium sulphate insoluble in HCl .



(iii) When a solution of potassium bromide is shaken with chlorine water, bromine is set free. The liberated bromine on shaken with carbon disulphide, dissolves in the latter and the carbon disulphide layer is coloured brown.

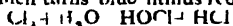
Iodine is also similarly liberated from potassium iodide. Iodine dissolves in carbon disulphide giving a violet solution.

(5) *Chlorine possesses remarkable bleaching properties*: A dry green leaf, a red flower and a piece of litmus paper are introduced into a dry gas jar filled with dry chlorine. It will be observed that the colour of each of the materials remains unchanged. But all the materials inside the jar are bleached when a little water is added to the jar. This proves that dry chlorine does not bleach dry colouring matter. But the moist chlorine bleaches all vegetable colours.

It is to be noted that moist chlorine cannot bleach printed papers. The printer's ink contains free carbon which is not attacked by chlorine. Chlorine has no action on papers carrying lead pencil marks.

It has been observed that when a piece of moist blue litmus paper is held in chlorine gas the litmus paper first turns red and then becomes colourless. The change of colour may be explained thus

Chlorine first reacts with moisture (water) producing hypochlorous acid and hydrochloric acid which turns blue litmus red



The red colour thus formed is next bleached by chlorine as usual.

Uses: (a) In the sterilisation of water, chlorine is used as a disinfectant. (b) Chlorine is extensively used as a bleaching agent in paper and textile industries. (c) It is also used in the manufacture of bleaching powder, chloroform, gamoxen, D D T, bromine, many metallic chlorates and chlorides. At present, chlorine finds its application in the commercial production of hydrochloric acid by synthetic method. (d) Many poison gases, such as phosgene, mustard gas, chloropicrin are prepared with the help of chlorine. Sometime, chlorine itself is used as a poison gas. (e) It is used in the extraction of gold.

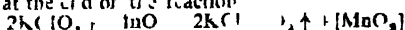
Tests: (a) Chlorine can be detected by its greenish yellow colour and peculiar irritating smell.

(b) When a piece of paper moistened with a starch potassium iodide solution is held in chlorine, the paper turns blue. This is a very reliable test for identification of chlorine. Chlorine liberates iodine from potassium iodide and the iodine produces a blue colouration with starch.



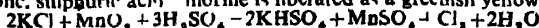
Proof of the presence of oxygen and chlorine in potassium chlorate

Oxygen When a mixture of potassium chlorate and manganese dioxide is heated in a hard glass test tube, potassium chlorate decomposes to produce potassium chloride and oxygen. Manganese dioxide acts as a catalyst and remains unchanged at the end of the reaction.



That the gas coming out of the tube is oxygen is proved by the fact that it rekindles a glowing chip of wood.

Chlorine The residue left in the test tube after the removal of oxygen is a mixture of potassium chloride and manganese dioxide. When the mixture is heated with conc. sulphuric acid, chlorine is liberated as a greenish yellow gas,



The gas turns starch potassium iodide paper blue. This test clearly confirms that the evolved gas is chlorine.

BROMINE

Symbol Br	Formula Br ₂	At. wt. 79.916
Atomic number 35	Position in periodic Table VIIB	

Bromine is not found free in nature. It occurs chiefly as the bromides of potassium, sodium and magnesium in sea water and Stassfurt deposits in Germany.

Bromine was discovered by Balard in 1826 by the action of chlorine on the mother liquor left after the crystallisation of common salt, (NaCl) from sea water. This liquor contained bromine as magnesium bromide.

Preparation : (A) Laboratory method : In the laboratory, bromine is prepared by carefully heating a mixture of potassium bromide (or sodium bromide), manganese dioxide and concentrated sulphuric acid.



An intimate mixture of potassium bromide, manganese dioxide and fairly strong sulphuric acid is taken in a stoppered glass retort which is placed on a wire gauze and clamped with the stand. The long end of the retort is introduced into a round bottomed flask kept cooled by a stream of water.

On heating the retort cautiously, bromine is liberated as a red gas and condenses to a dark red liquid in the cooled flask acting as a receiver.

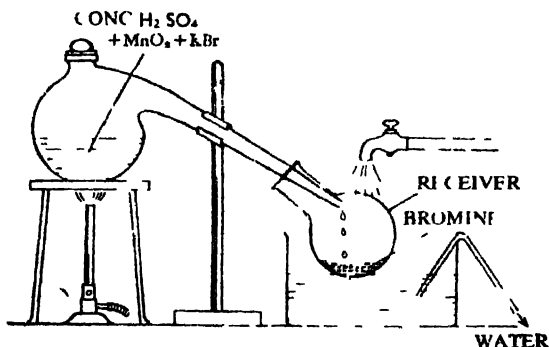


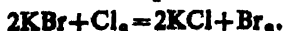
Fig. 2(48) Preparation of bromine in the laboratory

N.B. Bromine may be obtained by heating potassium bromide only with concentrated sulphuric acid. In this case, the hydrogen bromide initially formed by the action of potassium bromide on concentrated sulphuric acid gets oxidised to bromine by the acid.



Addition of manganese dioxide facilitates the reaction.

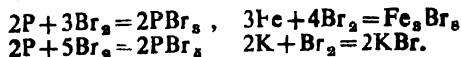
(B) Bromine can also be prepared by passing chlorine into a concentrated solution of potassium bromide.



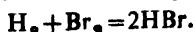
Properties : Physical—(1) At the ordinary temperature, bromine is a deep red liquid. Although it boils at 59°C , the liquid is very volatile and rapidly gives off red vapours. Bromine is the only non-metal which is a liquid at the ordinary temperature. (2) Bromine is a heavy liquid (sp gr. 3.15) (3) It has a strong pungent and suffocating odour. It is highly poisonous. The bromine vapour easily attacks the eyes, nose and throat. The liquid bromine corrodes the skin severely. (4) It is slightly soluble in water, and the aqueous solution is reddish in colour. It is highly soluble in organic solvents like chloroform, alcohol, ether, carbon disulphide giving reddish brown solution.

Chemical : Bromine shows close similarity with chlorine in chemical behaviour but it is less active than chlorine.

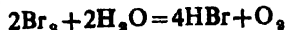
(1) *Bromine vapours are not combustible and ordinarily do not support combustion*. But many non-metals and metals burn spontaneously in bromine vapour. It reacts with many non-metals (except carbon, nitrogen and oxygen) yielding the respective bromides. Metallic potassium burns with explosion yielding potassium bromide.



(2) *Bromine has lesser affinity for hydrogen than chlorine*. Bromine and hydrogen do not combine at the ordinary temperature. Bromine unites slowly with hydrogen in sunlight but reacts with hydrogen easily when heated yielding hydrogen bromide. Here, bromine behaves as an oxidising agent.



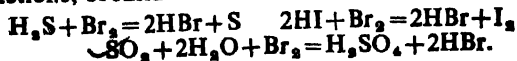
(3) Bromine is slightly soluble in water giving a reddish solution known as *bromine water* which is fairly stable in the dark but decomposes to produce oxygen in the bright sunlight



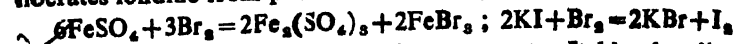
Saturated aqueous solution of bromine, on cooling in ice, separates different crystalline bromine hydrates, such as,



(4) *Bromine acts as an oxidising agent* but its oxidising action is milder than that of chlorine. It oxidises hydrogen sulphide to sulphur, hydrogen iodide to iodine and aqueous solution of sulphur dioxide (sulphurous acid) to sulphuric acid. In each of the above reactions, bromine is reduced to hydrogen bromide.



Bromine can oxidise ferrous sulphate to ferric sulphate and liberates iodine from potassium iodide by oxidation.

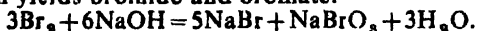


Bromine possesses feeble bleaching property. It bleaches litmus.

(5) *Bromine resembles chlorine in its action upon alkalis. It reacts with an excess of cold and dilute solution of an alkali (caustic soda or caustic potash) yielding a mixture of bromide and hypobromite.*



Excess of bromine on being reacted with hot and strong alkali solution yields bromide and bromate.



Bromine reacts with alkaline hydrogen peroxide solution liberating oxygen.



(6) *It gives addition products with unsaturated compounds like ethylene etc. When ethylene is passed through bromine water, an addition-product named ethylene dibromide is formed and the colour of bromine water is discharged. $\text{C}_2\text{H}_4 + \text{Br}_2 = \text{C}_2\text{H}_4\text{Br}_2$*

Experiments to illustrate the important properties of bromine :

(1) *Bromine is heavier than glass.* When a glass stopper is plunged into bromine taken in a beaker, the stopper is found to float on the surface of the liquid.

(2) *Bromine is soluble in carbon disulphide.* Carbon disulphide is added to bromine water taken in a test tube. When the content of the test tube is thoroughly shaken, bromine is found to dissolve in carbon disulphide producing a reddish brown solution.

(3) *Bromine is not inflammable and generally does not support combustion.* When a lighted taper is lowered in a jar of bromine vapour, the taper is extinguished and the bromine vapour does not burn.

But a burning jet of hydrogen continues to burn in bromine vapour giving hydrogen bromide $\text{H}_2 + \text{Br}_2 = 2\text{HBr}$.

If a little arsenic powder is dusted in a jar of bromine vapour, arsenic burns spontaneously with reddish white flame yielding arsenic bromide. $2\text{As} + 3\text{Br}_2 = 2\text{AsBr}_3$

A piece of moist litmus paper is slowly bleached when placed in a gas-jar containing bromine vapour.

Uses : (1) Bromine is extensively used in the preparation of various useful bromides like potassium bromide, silver bromide etc. Silver bromide finds its application in photography and potassium bromide is used in medicine as a hypnotic.

(2) Bromine is also employed in the manufacture of organic dyes, methyl bromide (used as a fire extinguisher), ethylene dibromide (used as an antiknock agent in petrol), lead tetra ethyl (used in petrol) and tear gases.

(3) Bromine is used in the bromination and oxidation of organic compounds.

(4) Sometimes, bromine is used as a disinfectant. For this purpose, kieselghur is saturated with bromine and sold under the trade name solid bromine. (bromum solidificatum).

Tests : (1) Bromine can be detected by its deep red colour and irritating smell. (2) It turns starch solution orange-yellow. (3) A piece of paper soaked in starch potassium iodide solution is turned blue by bromine. (4) When shaken with carbon disulphide or ether, bromine dissolves in the liquid imparting to it a reddish brown colour.

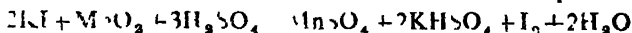
IODINE

Symbol I,	Mol. formula I_2 ,	At. weight 126.92
Atomic number 53	Position in periodic table VIIB	

Iodine does not occur free in nature. It is found in nature in combination with some metals. Some iodine compounds are found in sea water, sea weeds and sea animals. It occurs in small quantity as sodium iodate which is associated with Chile saltpetre. Iodine is also present in cod liver oil in the thyroid glands of animals and in milk in very minute amount.

In 1812, Courtois discovered the element from the ash (kelp) produced by burning sea-weed. Gay Lussac named it iodine for its violet colour. Greek word *iodid* means violet.

Preparation (A) Laboratory method In the laboratory, iodine is prepared by heating a mixture of potassium iodide (or sodium iodide), manganese dioxide and concentrated sulphuric acid.



A mixture of potassium iodide, manganese dioxide and concentrated sulphuric acid is taken in a dry glass vessel, the end of which is connected to water-cooled receiver-bottomed flask acting as a receiver. The mixture is then carefully heated when iodine is set free. Iodine is collected as violet vapours which condense in the cooler part of the receiver and fall in the receiver as shining black crystals.

The crude product is then mixed with solid potassium iodide and sublimed when pure iodine is obtained.

Bromine may also be prepared by passing chlorine gas into a strong solution of potassium iodide. $2KI + Cl_2 \rightarrow 2KCl + I_2$

Properties. Physical (1) At ordinary temperature, iodine is a dark grey crystalline solid with a metallic lustre.

(2) It is directly transformed into violet vapours on heating. When heated to above $700^\circ C$ iodine undergoes thermal dissociation and its diatomic molecules are converted into monatomic molecules.



(3) It is very slightly soluble in water but fairly soluble in organic solvents like alcohol, carbon disulphide, chloroform, ether etc. The colour of the solutions differs with different solvents. (4) Its density is 4.9.

Chemical : Of the halogens, iodine is the least active element but shows close resemblances with chlorine and bromine in chemical properties.

(1) Iodine unites directly even at ordinary temperature, with phosphorus, chlorine, bromine, mercury etc. producing the respective iodides.



$I_2 + 3Cl_2 = 2ICl_3$ (Iodine trichloride, a yellow crystalline solid)

$I_2 + Cl_2 = 2ICl$ (Iodine monochloride, a red solid)

$I_2 + Br_2 = 2IBr$ (Iodine monobromide, a black solid)

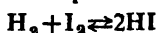
If a mixture of iodine and mercury is rubbed in a mortar, green mercuric iodide and red mercurous iodide are formed. The nature of the iodide formed depends on the quantity of mercury used.

$2Hg + I_2 = Hg_2I_2$ (when mercury is in excess)

$Hg + I_2 = HgI_2$ (when iodine is in excess)

(2) The iodine vapours do not burn but support the combustion of white phosphorus, arsenic, antimony etc. The combustion of these substances in iodine vapours takes place less energetically.

(3) The affinity of iodine for hydrogen is less than that of chlorine or bromine. It does not combine readily with hydrogen. Combination between the two elements takes place on heating in presence of a catalyst like platinum or tungsten.



(4) Iodine is practically insoluble in water but is highly soluble in an aqueous solution of potassium iodide giving a brown solution due to the formation of potassium tri-iodide.

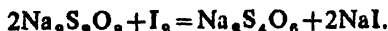


Thus, iodine cannot be separated from a mixture of iodine and potassium iodide by dissolving the soluble iodide in water. Iodine from such a mixture is separated by the process of sublimation.

(5) Iodine possesses mild oxidising properties. When hydrogen sulphide is passed into a suspension of iodine in water, the former is oxidised to sulphur by iodine. Iodine oxidises the aqueous solution of sulphur dioxide (sulphurous acid) and a sulphite solution to sulphuric acid and a sulphate respectively. In each case, iodine itself is reduced to hydroiodic acid.



Iodine reacts with sodium thiosulphate giving sodium tetrathionate and sodium iodide. In this case, the colour of iodine gets discharged.



As iodine is insoluble in water, it has no bleaching property.

(6) Iodine resembles chlorine or bromine in its action upon alkalis. With excess of a cold, dilute solution of an alkali (sodium hydroxide, potassium hydroxide), iodine produces iodide and hypoiodite.

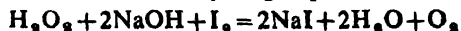


Excess of iodine on being reacted with a hot and concentrated alkali solution gives iodide and iodate.

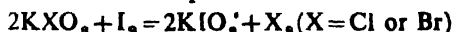


The hypoiodites are very unstable compounds and pass into iodates and iodides simply on standing.

Iodine dissolves in alkaline hydrogen peroxide evolving oxygen.



(7) Iodine cannot displace chlorine or bromine from a chloride or a bromide. However, iodine can displace chlorine or bromine from potassium chlorate or potassium bromate.



(8) Iodine is the only halogen which can be oxidised by concentrated nitric acid to iodic acid



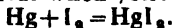
(9) The electronegative character of the halogens gradually decreases with increasing atomic weight. Thus, although being a non-metal, iodine behaves like an electropositive element in some of its compounds, such as,

ICI —iodine monochloride, ICl_3 —iodine trichloride
 ICN —iodine cyanide etc.

(10) Iodine produces an intense blue colour with starch solution. The colour disappears on heating but reappears on cooling.

Experiments to illustrate some of the properties of iodine :

(1) *Iodine directly combines with mercury, white phosphorus and arsenic giving the corresponding iodides* Mercury mixed with excess of iodine is rubbed in a mortar when yellowish red mercuric iodide is formed.



When a piece of white phosphorus is kept in contact with iodine in a porcelain basin, phosphorus first melts and then reacts so vigorously that the mixture bursts into flame. $2\text{P} + 3\text{I}_2 = 2\text{PI}_3$.

If antimony powder is sprinkled into a jar of iodine vapour, antimony takes fire at once. $2\text{Sb} + 3\text{I}_2 = 2\text{SbI}_3$.

(2) A little iodine is added to starch solution when a deep blue colouration is produced. The blue colour disappears on heating but reappears on cooling. The blue solution becomes permanently colourless on adding ammonium hydroxide.

(3) Iodine is highly soluble in potassium iodide solution. A few crystals of iodine are shaken with water taken in a test tube. The element practically remains undissolved. On adding potassium iodide into the test tube, iodine readily dissolves giving a brown solution.

(4) It gives off its vapour directly when heated. When some crystals of iodine are dropped into a heated flask, the flask is filled with violet vapours of iodine in no time. A piece of paper moistened with starch solution turns blue in the vapours.

Uses : (1) Iodine finds considerable use in medicine. It is an excellent disinfectant and is much used for the treatment of small wounds as tincture of iodine, a 10% solution of iodine in potassium iodide and alcohol.

(2) It is employed in the manufacture of certain dyes, iodoform and potassium iodide. Potassium iodide is used in photography and iodoform as an antiseptic in dressing wounds.

(3) It is also used in volumetric analysis.

(4) As a mild oxidising agent, iodine is used in organic syntheses.

Tests : (1) Iodine produces violet vapours when its crystals are dropped in a hot flask.

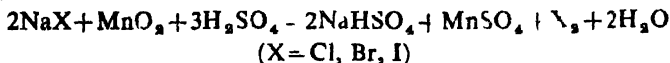
(2) Iodine produces an intense blue colouration with starch solution. This is a very characteristic test for iodine.

(3) It dissolves in carbon disulphide yielding a violet solution.

(4) It yields iodoform (a yellow, silky crystalline compound with characteristic smell) when it is warmed with ethyl alcohol or acetone and caustic soda solution.

Comparison between chlorine, bromine and iodine : Chlorine, bromine and iodine belong to the same family, closely related elements known as halogens. These elements have remarkable resemblances in properties and display a very well-justified gradation in their physical and chemical characteristics with increasing atomic weights.

Each of these elements is a non-metal. None of them is found free in nature. They occur in nature in combination with the metals. Three elements can be prepared in the laboratory by the application of a similar process.



They are all monovalent, highly electro-negative elements and their molecules are diatomic in the gaseous state.

The identical structure of the outermost electron layers of the three halogens accounts for their similarity both in their chemical behaviour and in the types and properties of the compounds they form.

Their atoms are characterised by an outer group of seven valency electrons, which, by receiving, a single electron, reach the stable inert gas type. Thus, they readily form ions with a single negative charge Cl^- , Br^- , I^- .

chlorine atom
[2. 8. 7]

chlorine ion
[2. 8. 8]⁻

The gradation in physical properties is tabulated below.

Physical property	Chlorine	Bromine	Iodine
Atomic weight	35.457	79.916	126.932
Atomic number	17	35	53
State of aggregation, colour, odour	Greenish yellow gas with irritating smell	Deep red liquid with extremely irritating smell	Dark, violet crystalline solid with metallic lustre. Violet in gaseous state.
Heaviness or sp gr.	2½ times heavier than air.	Sp. gr. 3.19 (liquid)	Sp. gr. 4.94 (solid)
Solubility in water	Fairly soluble	Less soluble than chlorine	Practically insoluble
Melting point	-102.4°C	-7.2°C	113.6°C
Boiling point	-34°C	58.2°C	184.5°C

It is to be noted that the density, melting and boiling points gradually increase with increasing atomic weight. The colour is also deeper with increasing atomic weight.

The chemical activity also increases with increasing atomic weight as follows:

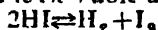
(a) Reaction with hydrogen. All the three elements unite with hydrogen to form hydrogen halides.



The affinity for hydrogen increases in the order: chlorine < bromine < iodine.

Chlorine does not react with hydrogen in the dark but mixture of hydrogen and chlorine explodes when exposed to bright sunlight. Bromine unites with hydrogen on exposure to sunlight. Iodine does not combine readily with hydrogen. A combination between them occurs partially on heating in presence of a catalyst like platinum.

The stability of the hydrogen halides increases gradually from hydrogen chloride to hydrogen iodide but the reducing power increases according to this order. Of these hydrides, hydrogen iodide is the least stable and dissociates even at lower temperature.



In aqueous solution, HCl, HBr and HI dissociate to a greater extent and are strong acids of about equal strength. Silver salts of all the three halogen hydrides are insoluble in water.

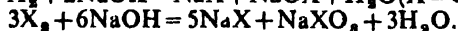
(b) Reaction with water. Chlorine decomposes water in bright sunlight yielding hydrochloric acid and oxygen.

Bromine decomposes water comparatively slowly when kept exposed to sunlight. Iodine has no action on water.



Chlorine and bromine react with ice-cold water forming crystalline halogen hydrates such as $\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Br}_2 \cdot 10\text{H}_2\text{O}$ etc.

(c) **Action on alkalis :** Chlorine reacts with a cold, dilute alkali solution giving chloride and hypochlorite ; with a hot and concentrated alkali solution, it produces a mixture of chloride and chlorate. Bromine and iodine give similar salts under identical conditions.



(d) **Reactions with non-metals :** Chlorine combines directly with many non-metals except oxygen, nitrogen and carbon. Bromine does not react with oxygen, nitrogen, carbon and silicon. Iodine can only unite with phosphorus, arsenic, hydrogen and other halogens.

(e) **Reactions with metals :** Almost all the metals are attacked by chlorine. Most of them burn in the gas giving metallic chlorides. Bromine attacks many metals but few of them burn in bromine vapours. Iodine combines with a few metals producing iodides.

(f) **Oxidising and bleaching properties :** The three elements are considered as oxidising agents ; their oxidising power decreases with increasing atomic weight. Similarly, the bleaching action diminishes from chlorine to iodine which has practically no bleaching power.

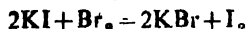
(g) The action of the halogens on starch solution is also remarkable.

Cl_2 + starch solution \rightarrow no change of colour

Br_2 + „ „ \rightarrow solution turns orange yellow

I_2 + „ „ \rightarrow solution turns intense blue.

(h) **Power of substitution :** Chlorine can displace bromine or iodine from a solution of a bromide or an iodide. Bromine can only replace iodine from an iodide solution. Iodine can never replace chlorine or bromine from a chloride or a bromide solution.



(i) **Power of forming oxides and oxyacids :** The three halogens chlorine, bromine and iodine can give rise to various oxides and oxyacids. The following oxides of chlorine are known.

Cl_2O , ClO_2 , Cl_2O_6 and Cl_2O_7 .

Bromine forms unstable oxides such as Br_2O , BrO_2 , Br_2O_3 etc. Comparatively stable iodine oxides— I_2O_4 , I_4O_9 , I_2O_5 etc. are known. Three halogens form oxyacids of the types HOX and HXO_3 . Chlorine and iodine can form per chloric acid HClO_4 and per iodic acid HIO_4 respectively. The stability of the oxyacids increases from chlorine to iodine. In the oxides and oxyacids, the halogens remain in various oxidation states varying from +1 to +7.

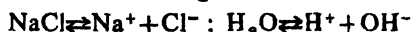
The electronegative character of the halogens gradually decreases with increasing atomic weight. In compounds like ICl , ICl_3 , iodine behaves like an electropositive element.

Manufacture of chlorine, bromine and iodine : Industrial methods of preparation of these three halogens have not been included in the syllabus. A brief account of the commercial processes is given here just to keep the students familiar with these processes.

Manufacture of chlorine : Chlorine is manufactured by three different processes.

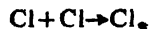
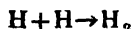
(A) **Electrolytic process :** Chlorine is at present manufactured almost exclusively by the electrolysis of brine (an aqueous solution of cheap and easily available sodium chloride). In fact, it is obtained as a by-product in the electrolytic production of sodium hydroxide and metallic sodium. Sea-water is used as a source of sodium chloride.

A concentrated solution of the salt (brine) is obtained by partial evaporation of the sea water. When electric current is passed through the brine using suitable electrodes, sodium chloride dissociates and liberates gaseous chlorine at the anode.



At the cathode, $\text{H}^+ + \text{e} \rightarrow \text{H}$

At the anode, $\text{Cl}^- - \text{e} \rightarrow \text{Cl}$



The chlorine obtained by the process is pure and concentrated.

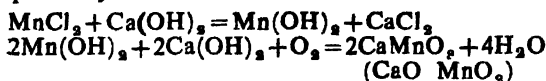
(B) **Weldon process .** The reaction of the process is similar to that taking place in the laboratory method of preparation. Pyrolusite (mineral manganese dioxide containing about 10% ferric oxide) mixed with concentrated hydrochloric acid is heated by means of steam in heated stoneware stills. Chlorine is evolved and passes out through an exit pipe.



In this process, a part of hydrochloric acid is transformed into chlorine and the rest is used up to convert manganese dioxide into manganous chloride. The commercial success of this method depends on the fact that the manganous chloride is reconverted into manganese dioxide, which is then used again and again.

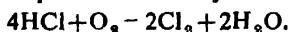
The spent liquor containing manganous chloride, ferric chloride (produced by the action of HCl on Fe_2O_3) and unreacted acid is taken in a tank and is mixed with lime stone. As a result excess of acid is neutralised and ferric chloride is precipitated as ferric hydroxide. The liquor is then allowed to settle down and the clear solution of manganous chloride from the top is taken to an iron cylinder where it is treated with excess of milk of lime. Steam and air are then blown through the mixture in such a way that the temperature remains at 60°C . Manganous chloride through a series of reactions is converted into calcium manganite which can be used to oxidise further quantity of hydrochloric acid. The manganite settles to the bottom as a dark coloured mud known

as *Woldon mud*. The reactions in the recovery of manganese dioxide are probably



The process gives chlorine in comparatively pure and concentrated form but the whole of hydrochloric acid is never oxidised to chlorine. This method is now obsolete.

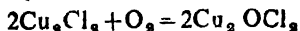
(c) **Deacon process** The process is based on the oxidation of gaseous hydrogen chloride at 450°C to chlorine by atmospheric oxygen in presence of anhydrous cupric chloride catalyst.



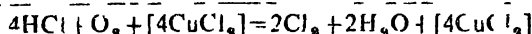
The mechanism of the catalytic reaction is



Cupric chloride Cuprous chloride



Copper oxychloride



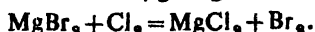
Cupric chloride is regenerated and the process goes on continually. Cuprous chloride formed acts as a carrier of oxygen.

This process produces much impure and diluted chlorine. But the chlorine can safely be used in the preparation of bleaching powder. This is also an out-of-date method.

Manufacture of bromine: Mineral carnallite $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ of Stassfurt deposit and sea-water are the sources for industrial production of bromine.

(A) **Bromine from carnallite** Carnallite contains about 1% magnesium bromide and a little sodium bromide.

The mother liquor left after the crystallisation of potassium chloride from the solution of powdered carnallite is commonly known as *bittern* and is found to contain 0.25% bromine as magnesium bromide. Bromine is extracted from the liquor by allowing the same to flow down a tower through which a stream of chlorine passes upward. These react, giving bromine.

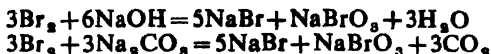


(B) **Bromine from sea water:** In U.S.A, bromine is nowadays recovered on a large scale from sea-water. Sea-water is acidified with sulphuric acid and saturated with chlorine when bromine is set free,

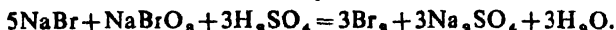


Bromine thus liberated is blown out by a current of air and is

absorbed in hot caustic soda or sodium carbonate solution. As a result, it forms soluble sodium bromide and sodium bromate



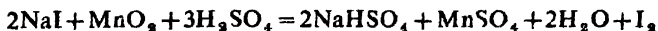
The resulting mixture of the two salts on acidification liberates free bromine which is carried out by steam.



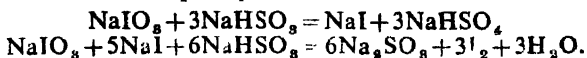
Manufacture of iodine :

(A) **From sea-weeds :** Dried sea-weeds are burnt and the resulting ash, called *kelp* contains about 1% iodine as sodium and potassium iodides. The kelp is extracted with hot water and is filtered to remove the insoluble matter. The filtrate is concentrated and cooled when the less soluble sodium and potassium sulphates, carbonates and chlorides crystallise out leaving the more soluble iodides of these metals in the mother liquor.

The concentrated mother liquor is then mixed with manganese dioxide and fairly strong sulphuric acid and heated in a cast iron retort. The liberated iodine sublimes and is collected in stone-ware receivers called *aludels*.



(B) **From Caliche :** Caliche or crude chile saltpetre (NaNO_3) contains about 0.2 per cent sodium iodate (NaIO_3) and is regarded as the main source of commercial iodine. The aqueous solution of caliche is concentrated and cooled when crystals of less soluble sodium nitrate separate out. The mother liquor left after removal of the nitrate becomes richer in iodate content. This is treated with calculated quantity of sodium bisulphite whereby iodate is reduced to iodine and is precipitated.



Iodine is separated by filtration and purified by sublimation.

OXIDES OF NON-METALS

Oxides of carbon : Carbon forms two important oxides namely carbon monoxide and carbon dioxide. Both the oxides are gases but they differ in almost all chemical properties.

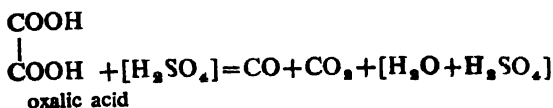
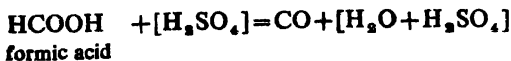
CARBON MONOXIDE

Mol formula CO	Boiling point -191.5°C
Mol. wt. 28.01	Melting point -200°C

Lassone in 1766 first prepared carbon monoxide by heating a mixture of carbon and zinc oxide. It is not found free in nature. Only minute traces of the gas occur free in air in the vicinity of volcanoes.

✓ **Preparation :** (A) By dehydration of formic acid or oxalic acid :

Laboratory method : Carbon monoxide is usually prepared in the laboratory by heating formic acid or oxalic acid with concentrated sulphuric acid. Concentrated sulphuric acid abstracts the elements of water from either of the organic acids giving carbon monoxide.



In the two reactions mentioned above, sulphuric acid remains unchanged and can be used again for conversion of further amount of formic or oxalic acid. But a minute quantity of sulphuric acid may be reduced to sulphur dioxide by the action of carbon monoxide evolved. $\text{H}_2\text{SO}_4 + \text{CO} = \text{H}_2\text{O} + \text{SO}_2 + \text{CO}_2$

Description of the method starting from formic acid : Concentrated sulphuric acid is taken in a round bottomed flask provided with a dropping funnel and a bent delivery tube. The free end of the delivery tube dips in concentrated caustic soda solution taken in a gas washer. Sulphuric acid in the flask is then heated to 100°C and formic acid is added to it carefully drop by drop from the dropping funnel.

A steady current of carbon monoxide is evolved on dehydration of formic acid. The evolved gas is passed through the caustic soda solution to remove traces of carbon dioxide and sulphur

dioxide and collected over water. Glacial phosphoric acid may be employed for dehydration instead of sulphuric acid.

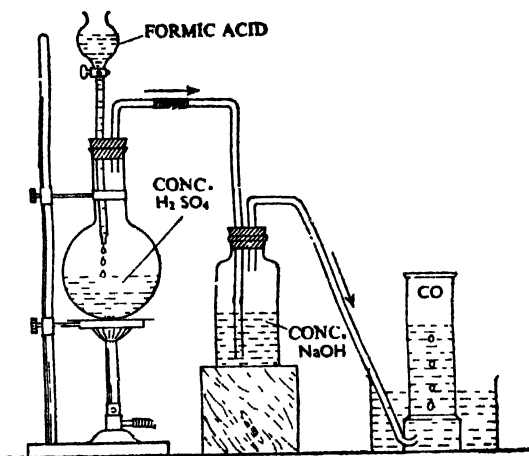


Fig. 2(49) Preparation of carbon monoxide in the laboratory

Description of the method starting from oxalic acid : Crystals of oxalic acid are taken in the roundbottomed flask and concentrated sulphuric acid is added to it from the dropping funnel. On heating the mixture in the flask to about 60°C , equal volumes of carbon monoxide and carbon dioxide are evolved. The issuing gases are passed through caustic soda solution in which carbon dioxide (including sulphur dioxide formed in minute amount) is absorbed and the carbon monoxide is collected by downward displacement of water. The gas may be dried by phosphorus pentoxide and collected over mercury.

The same apparatus as shown in Fig. 2(49) is used in this method. Instead of the dropping funnel, a thistle funnel may be employed. But one should be very careful to see that the end of the thistle funnel remains under the surface of sulphuric acid.

(B) Other methods :

(a) **From sodium formate:** Dry sodium formate on being slowly heated with concentrated sulphuric acid yields carbon monoxide. Conc. sulphuric acid first converts the formate to formic acid which is subsequently dehydrated to produce carbon monoxide.

$$\text{HCOONa} + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{CO} + \text{H}_2\text{O}$$

(b) **From carbon :** Carbon monoxide is also obtained by heating excess of carbon in a limited supply of air or by strongly heating a mixture of powdered calcium carbonate and carbon.

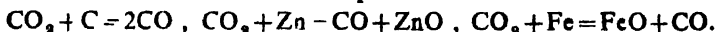


The blue flame observed above a coal fire is due to the combustion of carbon monoxide.

Carbon monoxide is produced by heating zinc oxide, lead oxide or iron oxide with carbon. The metallic oxide in each case is reduced to the metal.



(c) From carbon dioxide Carbon dioxide when passed over red hot charcoal, iron or zinc is reduced to carbon monoxide. The metals are oxidised to the respective oxides.



Method of preparation of carbon monoxide from carbon dioxide. A porcelain or iron tube packed with a layer of charcoal is heated

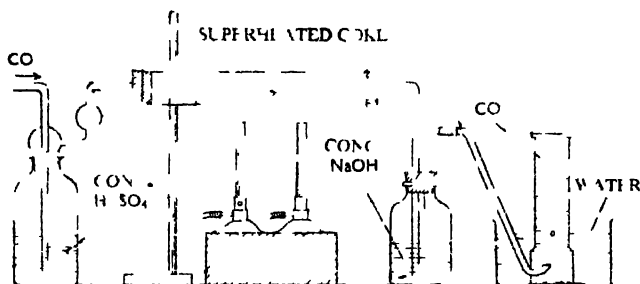
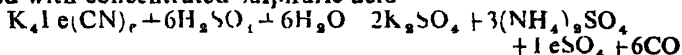


Fig. 2(50) Preparation of carbon monoxide from carbon dioxide

to redness in a furnace. A slow stream of carbon dioxide dried by passing through concentrated sulphuric acid is then led over the red-hot charcoal. The resulting carbon monoxide is freed from any unreacted carbon dioxide by bubbling it through strong caustic soda solution and is collected over water.

(d) Carbon monoxide is liberated when potassium ferrocyanide is heated with concentrated sulphuric acid



(e) Nickel tetracarbonyl on being heated decomposes to produce carbon monoxide $\text{Ni}(\text{CO})_4 = \text{Ni} + 4\text{CO}$

Nickel tetracarbonyl is an additive compound of carbon monoxide and nickel

Properties Physical—(1) Carbon monoxide is a gas with a peculiar faint smell. (2) It condenses to a colourless liquid at -191°C at ordinary pressure. (3) Carbon monoxide is very slightly soluble in water. (4) It is extremely poisonous. An atmosphere containing as little as 0.5% carbon monoxide may cause death if breathed for some time.

The fatal action of carbon monoxide is due to the fact that it combines with haemoglobin the oxygen carrier of blood forming a stable compound, carboxy haemoglobin. Thus the normal functioning of blood in the living system is stopped. Gas masks containing a mixture of manganese dioxide and cupric oxide are employed against carbon monoxide poisoning.

(4) It is slightly lighter than air.

Chemical : (1) Carbon monoxide is a *combustible gas but is a non-supporter of combustion*. It burns in air or oxygen with a pale blue flame giving carbon dioxide. $2\text{CO} + \text{O}_2 = 2\text{CO}_2$.

This reaction is highly exothermic.

(2) *It is a neutral oxide* : It has no action upon litmus. Ordinarily, the gas does not react with an alkali like sodium hydroxide or potassium hydroxide. However, at 200°C and under pressure, it reacts with solid caustic soda yielding sodium formate.



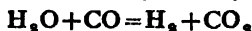
(3) *Carbon monoxide is a powerful reducing agent at elevated temperatures*. At red heat, it reduces many metallic oxides to the metals being itself oxidised to carbon dioxide.

When the gas is passed over red-hot cupric oxide, it reduces the oxide to red metallic copper and carbon dioxide is formed at the same time. $\text{CuO} + \text{CO} = \text{Cu} + \text{CO}_2$.

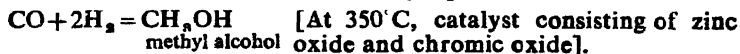
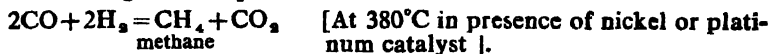
The gas will similarly reduce the oxides of zinc, iron, lead etc.



It reduces steam to hydrogen at 550°C in presence of a mixture of ferric oxide and chromic oxide (catalyst).



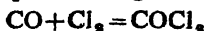
(4) At different temperatures and under the influence of different catalysts, carbon monoxide and hydrogen interact to give different organic compounds.



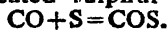
(5) Carbon monoxide directly combines with some non-metals and metals or some compounds giving additive products known as carbonyls.

Carbon atom is tetravalent. But carbon atom in carbon monoxide behaves like a divalent atom and as such the oxide is an unsaturated compound with the tendency of undergoing addition-reactions.

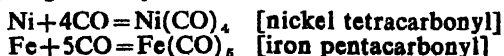
Carbon monoxide directly combines with chlorine in presence of sunlight or charcoal catalyst giving carbonyl chloride also called phosgene which is a highly poisonous gas.



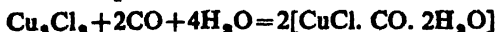
It also combines with heated sulphur vapour to form carbonyl sulphide.



Finely divided nickel at 40°C and iron at 120°C absorb carbon monoxide giving carbonyls.



Cuprous chloride in conc. hydrochloric acid or ammonium hydroxide absorbs carbon monoxide and a white crystalline precipitate is formed. In fact, it is an additive compound of carbon monoxide and cuprous chloride.

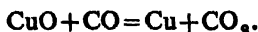


Traces of carbon monoxide present in carbon dioxide, hydrogen, nitrogen, nitric oxide etc. can be removed by bubbling through a solution of cuprous chloride in conc. hydrochloric acid which will absorb only carbon monoxide. The other gases will remain unchanged.

Experiment to illustrate that carbon monoxide possesses reducing property :

The mouths of a hard glass combustion tube are closed with bored corks fitted with an inlet and a bent outlet tube. The end of the outlet tube dips in clear lime water kept in a bottle. A small amount of black cupric is introduced into the combustion tube and carbon monoxide is slowly passed through the inlet tube. Now, the oxide inside the tube is strongly heated in a current of carbon monoxide. It is seen that cupric oxide is gradually reduced to red metallic copper by carbon monoxide. Carbon dioxide coming out of the outlet tube turns lime water milky. The unchanged carbon monoxide is burnt at the mouth of an outlet tube fitted with the bottle.

When the reaction is complete, passing of carbon monoxide is stopped and the combustion tube is cooled to the room temperature. The red residue inside the tube on being treated with concentrated nitric acid gives a blue solution with simultaneous evolution of a brown gas. So, the red substance is nothing but copper.



This experiment proves that carbon monoxide reduces cupric oxide to metallic copper and it itself is oxidised to carbon dioxide.

Uses : (1) As a constituent of water gas, producer gas, carbon monoxide is used as a fuel.

(2) It is used as a reducing agent in the extraction of metals. It finds its application in the purification of nickel.

(3) It is also used in the manufacture of synthetic methyl alcohol, synthetic methane and artificial petrol.

Tests : (1) When a lighted taper is introduced in a jar of carbon monoxide, the taper is extinguished but the gas burns with a lambent blue flame forming carbon dioxide which turns clear lime water milky.

(2) It is absorbed by a solution of cuprous chloride in conc. HCl or NH_4OH .

(3) It turns ammoniacal silver nitrate solution brown.

Minute traces of carbon monoxide in air may be detected by shaking with much diluted blood. If carbon monoxide is present it forms carboxy haemoglobin which

produces a red precipitate instead of a brown one given by a sample of normal blood.

It is to be noted that both hydrogen and carbon monoxide are combustible gases and burn in air giving pale blue flames. The product of combustion in case of hydrogen is water which turns white anhydrous copper sulphate blue.

But carbon monoxide on burning gives carbon dioxide which turns lime water milky.

CARBON DIOXIDE

Mol. formula CO_2	Boiling point— -56°C
Mol. weight 44.01	Sublimes at— -78.5°C

Carbon dioxide was discovered by Van Helmont in 1630 by burning wood and similar substances. He named it the *gas sylvestre*. In 1754, Black gave it the name *fixed air* by observing its solubility in water. Lavoisier, in 1783, first proved conclusively that it is an oxide of carbon and called it *carbonic acid gas* due to its acidic character.

In the free state, it occurs in the air to the extent of about 0.03 per cent by volume. The existence and the growth of plant kingdom depend on the atmospheric carbon dioxide. It occurs in many spring waters. It is found to come out in abundance from the interior of the earth in certain localities near volcanoes.

Preparation: (A) By the action of dilute mineral acids on metallic carbonates.

Laboratory method: In the laboratory, carbon dioxide is commonly prepared by the action of dilute hydrochloric acid on marble (calcium carbonate, CaCO_3) at the ordinary temperature.



Small pieces of marble are placed in a Woulfe's bottle fitted with a thistle funnel and a delivery tube. Some water is then added to the bottle so that the pieces of marble and the end of the thistle funnel remain dipped in water. Moderately strong hydrochloric acid is then poured down the funnel. As soon as the acid comes in contact with the marble, quick effervescence takes place due to the evolution of carbon dioxide which begins to come out through the delivery tube. As the gas is $1\frac{1}{2}$ times heavier than air, it is collected in the gas jar by the upward displacement of air.

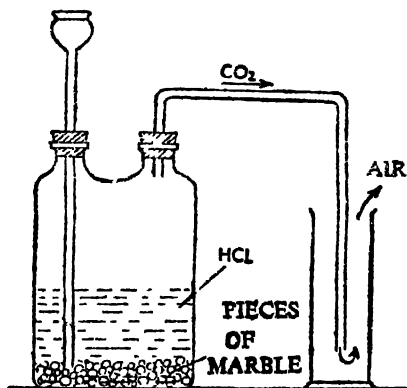
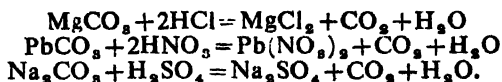


Fig. 2(51) Preparation of carbon dioxide in the laboratory

Carbon dioxide prepared in this way may contain some hydrochloric acid vapour and water vapour as impurities. The gas is

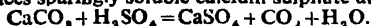
passed through a solution of sodium bicarbonate to free it from HCl vapour and then dried by conc. sulphuric acid. The pure and dry gas may be collected over mercury.

Other carbonates on treatment with dilute acids liberate carbon dioxide.



Preparation of carbon dioxide in Kipp's apparatus : When a ready supply of carbon dioxide is required, a Kipp's apparatus may be used for its generation. The description and working principle of the Kipp's apparatus have been given in connection with the preparation of hydrogen. For the preparation of carbon dioxide with the help of this apparatus, marble (CaCO_3) is taken in the central globe and dilute hydrochloric acid is poured down the funnel attached to the upper globe.

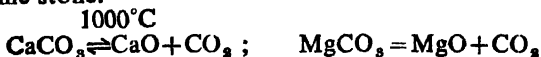
N.B. Dilute sulphuric acid is not used in the preparation of carbon dioxide from marble. Dilute sulphuric acid at first decomposes marble liberating carbon dioxide and produces sparingly soluble calcium sulphate at the same time.



This sulphate then forms an insoluble coating on the unreacted marble, thus preventing the same from coming in contact with the acid. As a result, the action soon stops and no carbon dioxide is evolved.

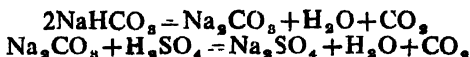
No such difficulty arises when hydrochloric acid is used as the calcium chloride produced is highly soluble.

(B) By thermal decomposition of metallic carbonates and bicarbonates : Almost all metallic carbonates except carbonates of alkali metals (Na_2CO_3 , K_2CO_3) and barium carbonate (BaCO_3) decompose to carbon dioxide and metallic oxides when heated strongly. Large quantities of carbon dioxide may be prepared by heating lime stone.

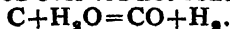


Carbon dioxide is obtained as a by-product in the manufacture of lime.

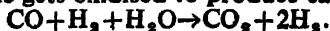
In the laboratory, pure carbon dioxide is best obtained by heating sodium bi-carbonate or by treating sodium carbonate with dilute sulphuric acid.



(C) Carbon dioxide may commercially be obtained from water gas. When steam is passed over red hot coke, water gas is produced.



If steam is led through the gas mixture in presence of catalysts, carbon monoxide gets oxidised to produce carbon dioxide.



The gas is freed from hydrogen and unreacted carbon monoxide by absorption in cold potassium carbonate solution forming potassium bicarbonate which gives off carbon dioxide on boiling.



(D) Besides, we get carbon dioxide by burning carbon, wood, coal, petrol, oil etc in excess of air. $C + O_2 = CO_2$

Properties—Physical : (1) Carbon dioxide is a colourless, odourless gas with a faint acid taste. The gas can be liquefied to a colourless liquid under a pressure of 60 atmospheres at ordinary temperature. Carbon dioxide in the liquid form is kept in steel cylinder. When liquid carbon dioxide is suddenly allowed to escape, it solidifies. This solid carbon dioxide looks like snow and is called 'dry ice'. It is used in low temperature investigations. When it is mixed with ether, a very low temperature up to $-140^\circ C$ is reached.

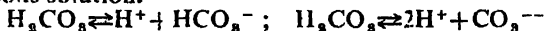
(2) It is $1\frac{1}{2}$ times heavier than air. This is why the gas is sometimes found to collect in many disused wells. (3) Carbon dioxide is fairly soluble in water. At ordinary temperature, water dissolves its own volume of the gas. The solubility of the gas increases with the increase of pressure. It is more soluble in alcohol than water. (4) It is not poisonous but does not support respiration of animals.

Chemical : (1) carbon dioxide is neither combustible nor a supporter of combustion. But ignited magnesium, sodium and potassium continue to burn in the gas with the separation of carbon and the burning metal is converted into either oxide or carbonate.



(2) Carbon dioxide is an acidic oxide. Its aqueous solution shows feeble acidic character due to the formation of carbonic acid. This is why it is called the anhydride of carbonic acid. It turns blue litmus solution slightly red but has no action on methyl orange indicator. $H_2O + CO_2 \rightleftharpoons H_2CO_3$.

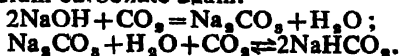
Carbonic acid is a weak, unstable dibasic acid and is known only in aqueous solution.



The acid can give rise to two types of salts—bicarbonates [$NaHCO_3$, $Ca(HCO_3)_2$] and carbonates [Na_2CO_3 , $CaCO_3$].

As an acidic oxide, it reacts with the basic oxides forming carbonates. $CO_2 + Na_2O = Na_2CO_3$; $CO_2 + CaO = CaCO_3$.

It is absorbed by alkalis. On passing gaseous carbon dioxide through a solution of caustic soda, we get water soluble sodium carbonate. With excess of carbon dioxide, the alkali produces sparingly soluble sodium bicarbonate which on heating is converted into sodium carbonate again.



When carbon dioxide is passed into clear lime water, the latter turns milky due to the formation of insoluble white calcium carbonate. $\text{CO}_2 + \text{Ca(OH)}_2 = \text{CaCO}_3 + \text{H}_2\text{O}$

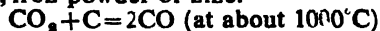
The milkiness disappears when excess of the gas is passed owing to the formation of soluble calcium bicarbonate.



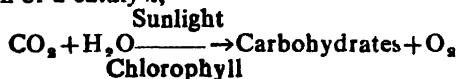
This clear solution on boiling turns milky again as the bicarbonate decomposes to produce insoluble calcium carbonate.



(3) Carbon dioxide is reduced to carbon monoxide by red-hot carbon, iron powder or zinc.



(4) In presence of sunlight and moisture, plants with the help of the green colouring matter, chlorophyll present mainly in their leaves can convert carbon dioxide into carbohydrates and oxygen. This process is known as photosynthesis. Chlorophyll does the function of a catalyst,



Experiments to illustrate some of the properties of carbon dioxide :

(1) *Carbon dioxide is neither combustible nor a supporter of combustion* but it supports the combustion of burning magnesium. A lighted taper is introduced in a gas-jar of carbon dioxide when the taper is extinguished and the gas in the jar does not burn.

A piece of ignited magnesium ribbon is held in a jar of carbon dioxide with the help of a pair of tongs. Magnesium is not extinguished but continues to burn with a bright flame. This proves that the gas is a supporter of combustion of burning magnesium,

As a result of burning, magnesium oxide and carbon are formed.



This experiment also proves that carbon dioxide is an oxidising agent at high temperature. It has oxidised metallic magnesium to its oxide and itself is reduced to elementary carbon.

(2) *It is not poisonous but does not support respiration.* A small mouse is introduced in a gas-jar of carbon dioxide and is covered with a lid. After some time, the mouse dies of suffocation.

(B) *Carbon dioxide is heavier than air :* (a) A jar of carbon dioxide is inverted over an empty jar (i.e. full of air) and the cover glass from the mouth of the latter is then removed. After a few minutes, it is found that carbon dioxide, being heavier than air, has travelled to the lower jar. When a lighted taper is introduced into the lower jar, the taper is extinguished at once. Clear lime water turns milky when added to the lower jar and shaken.

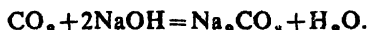
(b) A lighted candle is placed on a table and a jar of carbon dioxide is inverted over the candle flame. The flame is extinguished. Since the gas is heavier than air, it travels downwards and displaces air from the surroundings. The flame loses its contact with oxygen. Moreover, the gas is not a supporter of combustion and thus the lighted candle is extinguished. This experiment proves simultaneously that carbon dioxide is heavier than air and does not support combustion. It will clearly be understood from the nature of the flame as shown in the Fig 2(52).



Fig. 2(52)

(4) *Carbon dioxide is soluble in water and its aqueous solution is acidic.* A little water is added to a jar of carbon dioxide and shaken after covering the mouth of the jar with a lid. The jar is then kept inverted in a vessel containing water and the lid is removed. Water from the vessel is found to rise up gradually inside the jar and fills it almost completely. When blue litmus solution is added to the solution of the jar, it becomes dull red.

(5) *Carbon dioxide is absorbed by an alkali solution.* A few c.c. of sodium hydroxide solution is poured into a test tube filled with carbon dioxide. The tube is shaken on covering its mouth by the thumb and then inverted over water. Water rises up to fill the vacuum caused due to the absorption of carbon dioxide by the alkali. This experiment also proves the carbon dioxide is an acidic oxide.



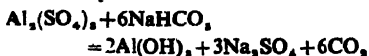
Uses : (1) Carbon dioxide is extensively used in the manufacture of sodium carbonate by Solvay's process, in the commercial production of salicylic acid and important fertilizers like urea, ammonium sulphate, (2) It is used in fire extinguishers. (3) It is used in the preparation of aerated water like soda water, lamonade etc. (4) Solid carbon dioxide finds wide use as refrigerant under the name 'dry ice'. (5) Liquid carbon dioxide is used for hardening of steel. (6) It is also used in medicine. A mixture of 95% oxygen and 5% carbon dioxide is administered to stimulate normal respiration of patients suffering from shock, carbon monoxide or similar gas poisoning.

The use of carbon dioxide in fire extinguishers has become very common nowadays. The fire extinguishers of different shapes are used. A fire extinguisher consists of a strong metallic vessel containing a solution of sodium carbonate with a glass bottle of sulphuric acid solution inside. When required, the bottle is broken by giving a blow to the knob attached to a rod which reaches to the bottle. As soon as the carbonate and the acid solutions come in contact with each other, the reaction sets in liberating carbon dioxide.



The mixture of the evolved gas and the liquid coming out forcibly from the nozzle is directed on the burning substances.

In extinguishing oil and petrol fires, 'foam' fire extinguishers are generally used. These contain a solution of aluminium sulphate or alum and sodium bicarbonate solution in separate receptacles. Aluminium sulphate being hydrolysed produces sulphuric acid which acts on sodium bicarbonate. When the solutions are mixed, a stable foam of bubbles of carbon dioxide is produced.



Aluminium hydroxide is formed causing the bubble walls stable. These extinguishers are effective for oil fires.

It is to be remembered that carbon dioxide cannot be used in extinguishing fire caused by the burning of magnesium as the gas is a supporter of combustion of this burning metal.

Tests : (1) A burning taper is extinguished in carbon dioxide gas. (2) It turns lime water milky.

It should be kept in mind that a lighted taper is also extinguished when introduced into a jar of nitrogen but nitrogen does not turn lime water milky.

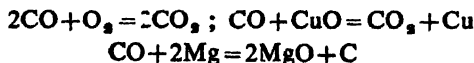
Conversion of carbon monoxide into carbon dioxide and vice versa. Carbon monoxide on burning in oxygen is oxidised to carbon dioxide. Carbon dioxide is also formed when carbon monoxide is passed over heated copper oxide, zinc oxide, lead oxide etc.



Preparation of carbon monoxide from carbon dioxide has already been described.

To prove that carbon monoxide and carbon dioxide contain carbon

If carbon monoxide gas is burnt in excess of pure oxygen or is passed over red-hot cupric oxide taken in a hard glass combustion tube, the gas is oxidised to carbon dioxide. A piece of ignited magnesium when introduced in the resulting gas, continues to burn in it. Magnesium oxide is produced with the separation of black carbon particles. The residue is then treated with hot dilute hydrochloric acid when the magnesium oxide gets dissolved leaving behind carbon. Carbon particles are filtered, washed, dried and burnt in oxygen. The gas produced on burning turns lime water milky. This proves that carbon dioxide has been produced and the black substance is nothing but carbon.



This experiment proves simultaneously the presence of carbon in both carbon monoxide and carbon dioxide.

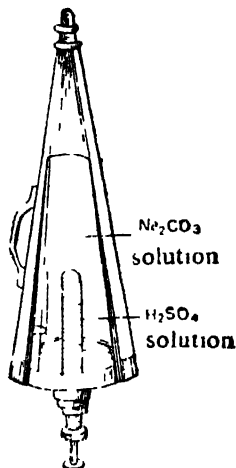


Fig (52A)
Fire extinguishers

Comparison of the properties of carbon monoxide and carbon dioxide :

Property	Carbon monoxide	Carbon dioxide
Physical state, nature, solubility in water etc.	Colourless, poisonous gas with peculiar faint smell, slightly lighter than air, almost insoluble in water. Liquefies at -193°C under ordinary pressure.	Colourless, odourless gas with a faint acid taste. Heavier than air. Non-poisonous but not a supporter of respiration. Fairly soluble in water. Liquefies under pressure at ordinary temperature, can be converted into a solid at low temperature and high pressure.
Combustibility	Combustible, non supporter of combustion, burns in air or oxygen with a blue flame forming carbon dioxide. $2\text{CO} + \text{O}_2 = 2\text{CO}_2$	Non-combustible, does not support combustion ordinarily but supports the combustion of burning magnesium, sodium or potassium.
Action on water, solutions of alkalis	Neutral oxide, very slightly soluble in water. No action on litmus. At ordinary temperature, does not react with an alkali but forms sodium formate with strong solution of caustic soda on heating under pressure. $\text{CO} + \text{NaOH} = \text{HCOONa}$	An acidic oxide, forms an unstable, weak, dibasic acid called carbonic acid in aqueous solution which turns litmus solution slightly red. $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$ At ordinary temperature, reacts with an alkali solution giving carbonate and bicarbonate $2\text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 = 2\text{NaHCO}_3$
	No action on lime water.	Turns lime water milky, milkiness disappears on prolonged passing of the gas.
Oxidising and reducing properties.	Powerful reducing agent at high temperatures, reduces some metallic oxides to the metals, it itself being oxidised to carbon dioxide. $\text{CuO} + \text{CO} = \text{Cu} + \text{CO}_2$ $\text{ZnO} + \text{CO} = \text{Zn} + \text{CO}_2$	At ordinary temperature, does not possess any oxidising or reducing property although metallic magnesium, sodium, potassium burn in the gas to form the corresponding metallic oxides. $2\text{Mg} + \text{CO}_2 = 2\text{MgO} + \text{C}$

Property	Carbon monoxide	Carbon dioxide
Power of forming additive compounds.	<p>An unsaturated compound, forms additive compounds with some non-metals and metals.</p> $\text{CO} + \text{Cl}_2 = \text{COCl}_2$ $\text{Ni} + 4\text{CO} = \text{Ni}(\text{CO})_4$ <p>At 120°C, it reacts with iron forming $\text{Fe}(\text{CO})_5$ $\text{Fe} + 5\text{CO} = \text{Fe}(\text{CO})_5$</p>	<p>A saturated compound, forms no addition product.</p> <p>At high temperature, iron is oxidised by carbon dioxide.</p> $\text{CO}_2 + \text{Fe} = \text{FeO} + \text{CO}$
Absorbent	Absorbed in ammoniacal cuprous chlorine soln. or in cuprous salt soln. in HCl.	Absorbed in NaOH, KOH etc.

Carbon dioxide cycle : The atmosphere contains 21% oxygen and 0.03% carbon dioxide by volume. Though the proportion of carbon dioxide in the atmosphere is very small, still upon its presence the continued existence of life depends.

In nature, some processes are going on indefinitely whereby carbon dioxide is used up and returned to the air. These opposite natural processes take place in such a way that the proportion of carbon dioxide in the atmosphere is almost maintained constant. The whole process is a cyclic one and is known as *carbon dioxide cycle*.

The processes by which carbon dioxide of the atmosphere is removed are stated below.

(1) In daytime, the plants absorb large quantities of carbon dioxide from the air and convert it to carbohydrates (the plant foods) in presence of sun light by the action of water and the green colouring matter, chlorophyll, present in plants. An equal volume of oxygen is liberated in the air simultaneously. The process of carbon assimilation with subsequent formation of carbohydrates using the energy of sunlight is known as photosynthesis. Chlorophyll acts as a catalyst.

(2) Carbon dioxide is moderately soluble in water and the atmospheric carbon dioxide reacts with rain water forming carbonic acid which is washed down by rains to the sea and is converted into calcium and magnesium bicarbonates. This carbon dioxide is permanently lost as a result of formation, by various aquatic creatures,

of shells consisting of calcium carbonate. The vast beds of lime stone and chalk are derived from this source.

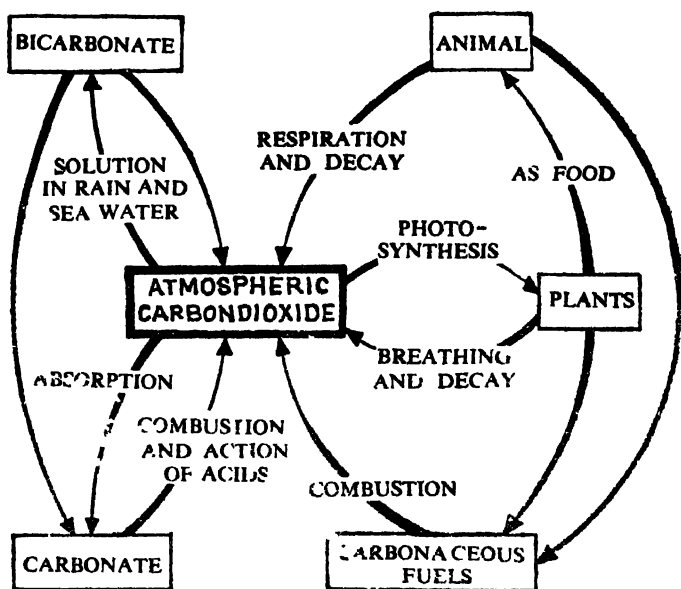


Fig. 2 53) Carbon dioxide cycle

(3) Carbon dioxide is an acidic oxide. Various rocks containing basic substances absorb a portion of the atmospheric carbon dioxide and convert the same to the metallic carbonates. This is known as 'weathering' of rocks.

The processes by which carbon dioxide are released into the atmosphere are as follows .

(1) Man and other animals give up carbon dioxide in the atmosphere on respiration. Plants take up carbon dioxide during day time for carrying out the process of photosynthesis but return carbon dioxide in the air at night as a result of respiration.

(2) Carbon dioxide is formed in nature due to the combustion of fuels such as wood, coal, oil, petroleum etc. It is to be noted that many plants are converted in course of time into coal, peat, petroleum etc. A vast quantities of carbon dioxide are released in the air as a result of decay of vegetable and animal matter.

(3) Carbon dioxide is also evolved from volcanoes and from minerals like lime stone, chalk, dolomite, marble etc. when these substances come in contact with organic acids present in the soil.

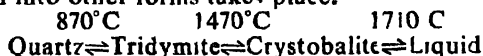
Carbon dioxide may also be liberated by the decomposition of bicarbonates in sea water.

The process of photosynthesis by plants and the other processes of using up atmospheric carbon dioxide act in opposite direction to respiration and combustion in such a way that the constancy in the proportions of oxygen and carbon dioxide in the air is maintained.

✓ SILICON DIOXIDE OR SILICA [SiO_2]

In nature, silica exists in both crystalline and amorphous forms. It enters into the composition of silicate minerals and rocks.

There are three definite varieties of crystalline silica known as quartz, tridymite and cristobalite. Quartz is the most widespread variety of silica. It is very stable up to 870°C . At higher temperatures, transformation into other forms takes place.



Quartz in its turn occurs in three forms—sand, amethyst and cat's eye.

Common sand consists of small particles of quartz left after weathering of rocks and crushed by water during its movements. Pure silica is a colourless solid but ordinary sand is usually grey or brownish due to the presence of ferric oxide or other metallic oxides.

Pure quartz is found as a colourless transparent crystalline substance and is called rock crystal. Frequently, many forms of quartz possess delightful colours due to the presence of small amounts of impurities and are used as gems. When manganese dioxide is present, the colour is pinkish and the quartz mixed with this oxide is called amethyst. The cat's eye consists of quartz containing a little dissolved asbestos.

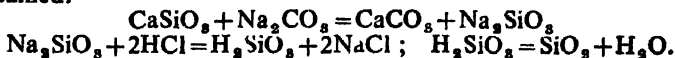
There are different types of amorphous silica such as opal, agate and flint of which opal is sometimes tinted yellowish brown. It is also used as a gem. Flint is a less pure form of amorphous silica and is coloured black or brown owing to the presence of iron oxide. Agate is a very hard substance and finds its use in mortars, knife edges. It was used as spear-heads in ancient times.

Silica not only occurs in the minerals but also in vegetable and animal organisms. The stems and exterior coatings of straw, bamboo, the quills of feathers contain appreciable quantity of silica. Kieselgurh consists of the fossil shells of the minute plants called diatoms. It is used as an absorbent for nitro-glycerine and as a polishing powder.

Preparation of silica : (A) In the laboratory, silica is prepared from a naturally occurring silicate.

The silicate mineral such as calcium silicate is fused with excess of sodium carbonate (or caustic soda) in a platinum crucible when

soluble sodium silicate is formed. The fused mass when cold is boiled with water and filtered. The filtrate is an aqueous solution of sodium silicate. The filtrate on acidification with conc. hydrochloric acid yields a gelatinous precipitate of silicic acid which is washed with water to free it from salts and HCl. Silicic acid is then dried and ignited, when pure amorphous silicon dioxide (silica) is obtained.



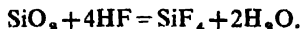
(B) Silica may also be obtained by burning silicon in air or oxygen. $\text{Si} + \text{O}_2 = \text{SiO}_2$

(C) Silicon tetra chloride on being treated with water gives a gelatinous precipitate of ortho silicic acid. The precipitate is filtered as usual, washed and dried. Dry ortho silicic acid decomposes at high temperature producing silica as amorphous powder.

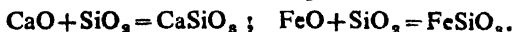


Properties : (1) Pure, crystalline silica is a colourless solid of sp. gr. 2.65. The sp. gr. of amorphous silica is 2.3. Quartz is a very hard substance while amorphous silica is relatively soft.

(2) All forms of silica are insoluble in water and resist the action of all acids excepting hydrofluoric acid (HF) which attacks it readily giving volatile silicon tetra fluoride. It is not attacked by aqua regia (a mixture of 3 vols. of conc. HCl and 1 vol. of HNO_3)

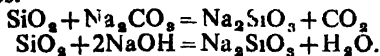


(3) Silica is an acidic oxide. At high temperatures, it combines with bases and metallic oxides forming silicates.



The acidic nature of silica is also confirmed by the following reactions.

When it is fused with sodium carbonate, effervescence of carbon dioxide takes place. Silica on being heated with strong alkalis produces silicates.



A colloidal solution of silicic acid is formed when excess of hydrochloric acid is added to a solution of sodium silicate in the cold.

When concentrated hydrochloric acid is added to sodium silicate solution at a temperature of 100°C or more, gelatinous mass called silica gel is produced. Silica gel, on being washed and dried, has a remarkable power of absorbing moisture. This is why it is used as a drying agent for gases. It is also used as an adsorbing agent and decolourising agent for some oils. This also finds its application as a catalyst.

(4) When an intimate mixture of silica and coke is heated to whiteness in a current of chlorine, silicon tetra chloride, a colour-

less fuming liquid is produced. Carbon monoxide evolves at the same time. $\text{SiO}_2 + 2\text{C} + 2\text{Cl}_2 = \text{SiCl}_4 + 2\text{CO}$

(5) A mixture of silica and excess of carbon when heated to $1500^\circ - 2000^\circ\text{C}$ in an electric furnace forms silicon carbide or carborundum which is a very hard substance. $\text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO}$.

(6) All varieties of silica begin to soften at about 1600°C and melt at the temperature of oxy-hydrogen flame (1700°C). Before melting, they are converted into plastic and may be worked and blown like glass.

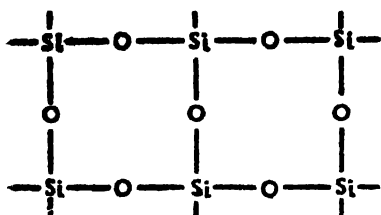


Fig. 2(54)

(7) Silica is not represented by a simple molecular structure. It is a 'giant molecule' formed by the union of a good number of its molecules. The structure of silica as shown in Fig. 2(54) is responsible for its extreme hardness.

Uses : (1) Transparent, colourless quartz or rock crystal is used for making lenses of optical instruments, spectacle lenses and prisms. Many of the coloured varieties of quartz are used as gems. (2) Silica is employed in making fire-proof, acid-proof interior linings of the furnaces used in the metallurgical operations. (3) It is used as a building material and in the preparation of glass, cement porcelain etc. Silica glass or quartz glass possesses certain remarkable properties such as infusibility, low coefficient of expansion, transparency to visible light, infra red and ultra violet rays, resistance to the attack of acids. It is, for such properties, used in the manufacture of electric instruments and various chemical apparatus. (4) Agate finds its use in making mortars, knife edges, in delicate instruments like chemical balances and watches. (5) Kieselgurh was formerly utilized in the manufacture of dynamite. Besides, it is used in making cement, refractory bricks and polishing powder.

Carbon dioxide and silica :

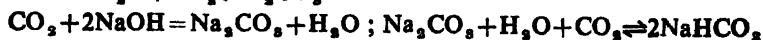
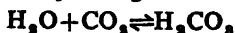
Carbon and silicon belong to the same family of elements. Carbon dioxide and silica are two typical oxides of these elements. Although the oxides are represented by the similar molecular formula RO_2 ($\text{R} = \text{C}$ and Si) and show very little resemblances in properties, they have notable differences in their physical and chemical characteristics.

Carbon dioxide exists as a single molecule having the structure $\text{O}=\text{C}=\text{O}$, but silica is a giant molecule having three-dimensional structure in which a silicon atom is tetrahedrally bonded with four oxygen atoms [Fig. 2(54)]

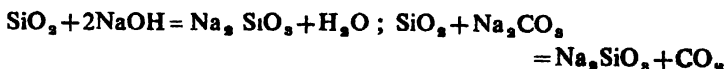
At ordinary temperature, carbon dioxide is a gas having little attraction between individual molecules. But silica in different

crystalline and amorphous forms is a hard solid substance with high melting point.

Both oxides are weak acidic oxides; carbon dioxide is more acidic than silica. Carbon dioxide is fairly soluble in water producing the weak carbonic acid known in solution only. It reacts easily with alkalis yielding carbonates and bicarbonates.



Silica is insoluble in water and in all acids excepting hydrofluoric acid. As an acidic oxide, it reacts with fused alkalis and sodium carbonate giving silicates.



Oxides of nitrogen : There are five oxides of nitrogen. In these oxides, nitrogen remains in various oxidation states.

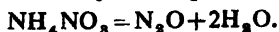
Name	Formula	Oxidn. No. of N
Nitrous oxide	N_2O	+1
Nitric oxide	NO	+2
Dinitrogen trioxide	N_2O_3	+3
Dinitrogen tetroxide or nitrogen dioxide	N_2O_4	+4
Nitrogen pentoxide	N_2O_5	+5

All the oxides of nitrogen are gases at ordinary temperature except nitrogen pentoxide (N_2O_5) which is a white solid.

NITROUS OXIDE OR LAUGHING GAS [N_2O]

Priestley discovered this gaseous oxide of nitrogen in 1772.

Preparation : (A) **Laboratory method**—In the laboratory, nitrous oxide is prepared by heating dry ammonium nitrate cautiously. The nitrate thermally decomposes giving nitrous oxide and water.



Dry ammonium nitrate is taken in a flask fitted with a cork through which passes a delivery tube.

On careful heating, ammonium nitrate first melts and then decomposes to produce nitrous oxide which comes out through the delivery tube and is collected by the downward displacement of hot water. It is not collected over cold water due to its appreciable solubility in it but may be collected over mercury.

The gas thus obtained contains nitric oxide, nitrogen dioxide,

ammonia, nitrogen and moisture etc in small amounts as impurities.

The gas is purified by passing successively through—

(i) caustic soda solution to remove nitrogen dioxide

(ii) ferrous sulphate solution to absorb nitric oxide

(iii) conc sulphuric acid to remove moisture and ammonia. The pure and dry gas is collected over mercury. It may however contain a little nitrogen.

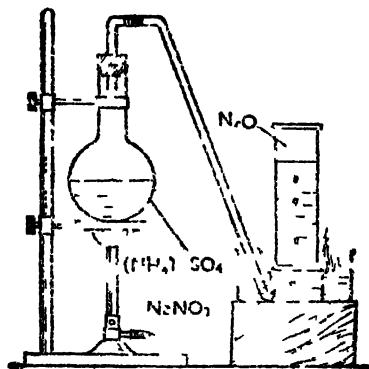
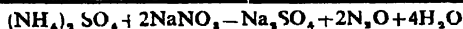
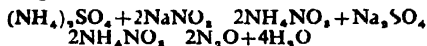
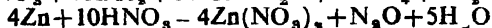


Fig 2(35) Preparation of nitrous oxide in the laboratory

mixture of ammonium sulphate and sodium nitrate. The ammonium nitrate produced by the double decomposition of the two salts undergoes decomposition as usual yielding nitrous oxide.

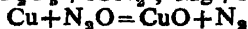
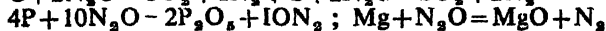


(B) Nitrous oxide may also be obtained by reducing nitric oxide with sulphur dioxide or nitric acid by stannous chloride in hydrochloric acid solution. The action of metallic zinc on dilute nitric acid leads to the evolution of nitrous oxide.

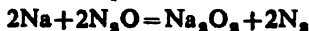


Properties : Physical—(1) Nitrous oxide is a colourless gas with a faint, pleasant odour. (2) It can be liquefied to a colourless liquid by the application of high pressure and low temperature (b.p. -88.5°C). (3) It is about $1\frac{1}{3}$ times heavier than air. (4) It is fairly soluble in water and more so in alcohol but insoluble in hot water.

Chemical (i) Nitrous oxide is a neutral oxide. (2) It is not inflammable but supports combustion like oxygen. It rekindles a glowing chip of wood. When pieces of burning charcoal, sulphur, phosphorus, magnesium, iron wire or heated copper are introduced in a jar of nitrous oxide, the substances continue to burn in the gas brilliantly. In each case, nitrogen and the oxide of the respective element are formed.



Heated sodium or potassium burns in the gas brightly producing nitrogen and the metallic peroxide.



In fact, heat produced during burning of the substances decomposes nitrous oxide into its elements—nitrogen and oxygen of which the latter one supports combustion. $2\text{N}_2\text{O} = 2\text{N}_2 + \text{O}_2$

(4) The gas has a remarkable action on the human system. It causes hysteric laughter when inhaled. This is why it has been given the name *laughing gas*. Inhalation of the gas for a considerable period of time causes anaesthesia and prolonged inhalation may finally cause death.

Uses : It is used as a mild anaesthetic, specially in dental and minor surgical operations.

Comparison of nitrous oxide and oxygen :

Both nitrous oxide and oxygen are colourless gases. Both of them are non-combustible but supporter of combustion. Oxygen on being reacted with nitric oxide at ordinary temperature produces reddish brown fumes of nitrogen dioxide. But nitrous oxide has no action on nitric oxide.



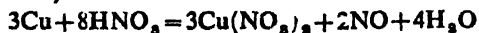
Oxygen is readily absorbed in alkaline pyrogallate solution giving a brown solution but nitrous oxide remains unaffected when passed through such a solution.

Ammoniacal cuprous chloride solution absorbs oxygen and the colour of the solution becomes blue. The same solution is without action on nitrous oxide.

—NITRIC OXIDE [NO]

This gas was discovered by Priestley in 1772.

Preparations : (A) Laboratory method : In the laboratory, nitric oxide is prepared at the ordinary temperature by the action of copper turnings on moderately concentrated (1 vol of the acid + 1 vol of water) nitric acid.



Pieces of copper turnings are taken in a Woulfe's bottle fitted with a thistle funnel and a delivery tube. Care must be taken to see that the apparatus used is perfectly air-tight. Now, a mixture of equal volumes of conc. nitric acid and water is poured down the funnel in such a way that the end of the thistle funnel and the copper turnings remain dipped under the surface of the liquid. As soon as the acid comes in contact with the metal, the reaction sets in with the

evolution of nitric oxide which at first produces reddish brown

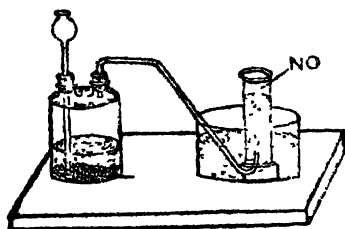


Fig. 2(56) Preparation of nitric oxide in the laboratory

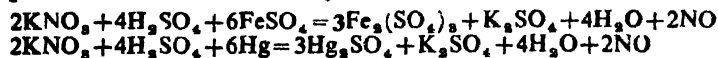
fumes of nitrogen dioxide with the air present in the bottle. To remove the brown fumes, nitric oxide is allowed to escape for sometimes and the colourless gas is then collected by the downward displacement of water.

The gas thus produced contains some nitrogen and its other oxides as impurities. The gas is purified by passing the same through a cold, saturated solution of ferrous sulphate in

which nitric oxide alone is absorbed, forming a dark brown solution containing the additive compound $\text{FeSO}_4 \cdot \text{NO}$.

This brown solution on gentle heating gives nearly pure nitric oxide.

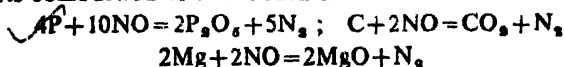
(B) Almost pure nitric oxide can be obtained by heating a mixture of dilute sulphuric acid, potassium nitrate and ferrous sulphate or by shaking a mixture of concentrated sulphuric acid potassium nitrate and mercury.



Properties : Physical—(1) Nitric oxide is a colourless gas, (2) It is slightly heavier than air (3) The gas is almost insoluble in water and cannot be liquefied easily.

Chemical : (1) It is a *neutral oxide*. (2) The compound is neither combustible nor does it ordinarily support combustion. It is a stable gas. Lighted candle, ignited taper, feebly burning sulphur or phosphorus are extinguished in the gas.

But nitric oxide decomposes at high temperature (about 1000°C) producing nitrogen and oxygen. $2\text{NO} = \text{N}_2 + \text{O}_2$. Hence, vigorously burning magnesium, phosphorus, carbon continue to burn in the gas forming the respective oxides. In these cases, oxygen liberated due to decomposition of nitric oxide at higher temperatures supports combustion of the elements.



(3) Nitric oxide is readily oxidised by oxygen. At ordinary temperature, it combines spontaneously with oxygen of the air to give brown fumes of nitrogen dioxide. $2\text{NO} + \text{O}_2 = 2\text{NO}_2$.

This is a characteristic test for both nitric oxide and oxygen.

(4) It tends to form addition products. In presence of charcoal (catalyst), nitric oxide combines with chlorine to yield the additive compound, nitrosyl chloride. $2\text{NO} + \text{Cl}_2 = 2\text{NOCl}$.

The gas is readily absorbed by cold ferrous sulphate solution giving rise to a dark brown, unstable nitroso compound $\text{FeSO}_4 \cdot \text{NO}$ in solution. This brown solution, on gentle heating, decomposes and nitric oxide is evolved. $\text{FeSO}_4(\text{NO}) \rightleftharpoons \text{FeSO}_4 + \text{NO}$.

This reaction is used in the ring test for detection of nitrites and nitrates.

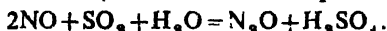
(5) When a gas-mixture of nitric oxide and hydrogen is passed through a hot tube containing platinised asbestos, nitric oxide is reduced to ammonia. $2\text{NO} + 5\text{H}_2 = 2\text{NH}_3 + 2\text{H}_2\text{O}$.

It is reduced to nitrogen when passed over heated sodium, potassium, iron, copper or nickel. $2\text{Cu} + 2\text{NO} = 2\text{CuO} + \text{N}_2$.

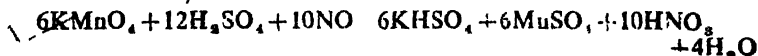
This reaction can be used to prove the presence of nitrogen in nitric oxide.

(6) A mixture of carbon disulphide vapour and nitric oxide burns with a blue flame. In this case, inflammable carbon monoxide is produced. $2\text{CS}_2 + 10\text{NO} = 2\text{CO} + 4\text{SO}_2 + 5\text{N}_2$.

In such reactions, nitric oxide acts as an oxidising agent. It also oxidises sulphurous acid to sulphuric acid.



(7) It possesses remarkable reducing properties. Nitric oxide reduces acidified solution of potassium permanganate to a colourless solution of manganous salt. While reducing, it is oxidised to nitric acid. Iodine also oxidises nitric oxide into nitric acid.



Uses : It is used as an oxygen carrier in the manufacture of sulphuric acid by Lead chamber process.

Tests : (1) It gives off brown vapours in contact with air. (2) It is absorbed in cold ferrous sulphate solution forming a deep brown solution.

NITROGEN TRIOXIDE [N_2O_3]

Preparation : Nitrogen trioxide may be obtained as red vapours on distilling a mixture of fairly concentrated nitric acid (6 %) and equal amount of arsenious oxide & starch. The red vapours condense to a deep blue liquid in a receiver kept immersed in a freezing mixture. A part of the oxide gets decomposed into nitric oxide and nitrogen dioxide at the time of its formation.



The compound is stable only in the liquid form.

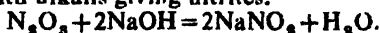
Properties : Physical—At ordinary temperature, it is a red gas when dry.

Chemical : (1) Nitrogen trioxide is not a stable compound. It dissociates with rise of temperature producing nitric oxide and nitrogen dioxide. $\text{N}_2\text{O}_3 \rightleftharpoons \text{NO} + \text{NO}_2$

(2) It is an acidic oxide. It is said to be the anhydride of nitrous acid as it forms the acid with ice-cold water.



It reacts with alkalis giving nitrites.



(3) Concentrated sulphuric acid absorbs the red gas with the formation of nitroso sulphuric acid

NITROGEN DIOXIDE [NO_2] or DINITROGEN TETROXIDE [N_2O_4]

Preparation : (A) From nitrates. **Laboratory method :** In the laboratory, nitrogen dioxide is prepared by strongly heating lead nitrate. The salt undergoes thermal decomposition giving gaseous nitrogen dioxide, oxygen and solid lead monoxide.

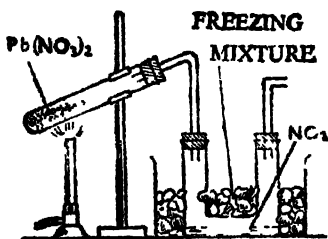


Fig. 2(57) Preparation of nitrogen dioxide

Powdered, dry lead nitrate is taken in a hard glass test tube fitted with a delivery tube. The delivery tube is connected with a U-tube cooled in ice-salt mixture. On gently heating the tube, nitrogen dioxide along with oxygen comes out of the delivery tube. Nitrogen dioxide condenses as a pale yellow liquid in the U-tube while oxygen passes out through the outlet.

The U-tube with its content is then kept in warm water when nitrogen dioxide evolves as a brown gas. It is collected in gas jars by downward displacement of air.

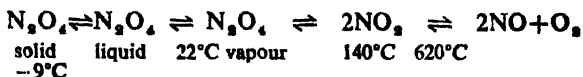
Many metallic nitrates (except sodium, potassium and silver nitrates) on strongly heating gives off nitrogen dioxide.

(B) From nitric acid : Concentrated nitric acid on being reduced by the metals like copper, zinc etc. produces nitrogen dioxide. The gas is also obtained when concentrated nitric acid is strongly heated.

(C) From nitric oxide : Nitric oxide combines with oxygen at the ordinary temperature yielding nitrogen dioxide. When a mixture of 2 volumes of nitric oxide and 1 volume of oxygen is slowly passed through a U-tube kept immersed in a freezing mixture, nitrogen dioxide is obtained as a liquid in the U-tube.



Properties : (1) Nitrogen dioxide is a poisonous gas with suffocating odour. (2) At ordinary temperature, it is deep brown in colour. On cooling in a freezing mixture, it condenses to a pale yellow liquid (b.p. 22°C). At -9°C , it solidifies to colourless crystals. Its molecular formula in the solid form corresponds to N_2O_4 . On heating, it is first converted into a yellow liquid and then to a brown gas at 22°C . With rise of temperature, the colour deepens gradually and at 140°C , N_2O_4 molecules completely dissociate into NO_2 molecules. Above 140°C , the colour becomes paler due to dissociation into nitric oxide and oxygen.



(3) *Nitrogen dioxide neither burns nor supports burning ordinarily.* A lighted taper is extinguished in the gas. But strongly burning phosphorus, sulphur, carbon and magnesium continue to burn brightly in the gas producing nitrogen and the oxides of the elements. The temperature of burning of these substances becomes so high that the gas decomposes into nitrogen and oxygen, the latter one supports the combustion.

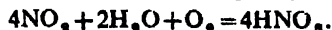


Potassium inflames in the gas spontaneously giving potassium nitrate and nitric oxide. $\text{K} + 2\text{NO}_2 = \text{KNO}_3 + \text{NO}$.

(4) *Nitrogen dioxide is an acidic oxide.* When dissolved in a small quantity of cold water, it produces a colourless solution of nitrous and nitric acids. Hence, it is called the mixed anhydride of these acids. $2\text{NO}_2 + \text{H}_2\text{O} = \text{HNO}_2 + \text{HNO}_3$.

With sufficient quantity of cold water or with hot water, it gives nitric acid and nitric oxide. $3\text{NO}_2 + \text{H}_2\text{O} = 2\text{HNO}_3 + \text{NO}$.

At ordinary temperature and in presence of excess of air, nitrogen dioxide reacts with water giving nitric acid only.



With an alkali solution (caustic soda or caustic potash), it gives rise to a mixture of nitrate and nitrite.



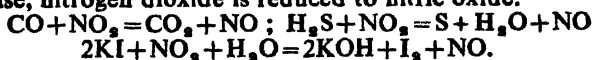
(5) Nitrogen dioxide possesses remarkable oxidising properties. It oxidises sulphur dioxide to sulphuric acid in presence of steam.



When nitrogen dioxide is passed over red-hot copper, the latter is oxidised to black cupric oxide and the gas is reduced to nitrogen. This reaction may be used to prove the presence of nitrogen in nitrogen dioxide.



It oxidises carbon monoxide to carbon dioxide, hydrogen sulphide to sulphur and liberates iodine from potassium iodide. In each case, nitrogen dioxide is reduced to nitric oxide.



(6) Concentrated sulphuric acid absorbs nitrogen dioxide with the formation of nitric acid and nitroso sulphuric acid, also known as nitrosyl sulphuric acid.



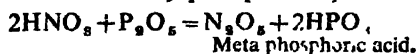
(7) It may be reduced to ammonia by hydrogen in presence of platinum. $2\text{NO}_2 + 7\text{H}_2 = 2\text{NH}_3 + 4\text{H}_2\text{O}$.

Uses : It is used in the preparation of nitric acid.

Tests : (1) The gas can easily be detected by its deep brown colour and pungent smell. It may be stated here that nitrogen dioxide and bromine vapours are identical in colour and odour. In order to distinguish between the two, the vapours are passed through water. Nitrogen dioxide gives a colourless solution containing nitrous and nitric acids while bromine dissolves in water giving a reddish solution. Nitrogen dioxide is not soluble in carbon disulphide whereas bromine is soluble in this solvent yielding a brown solution.

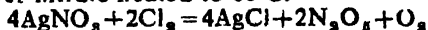
NITROGEN PENTOXIDE [N_2O_5]

Preparation : (A) Nitrogen pentoxide is prepared by dehydrating concentrated nitric acid by phosphorus pentoxide.



Phosphorus pentoxide is added to well-cooled concentrated nitric acid taken in a retort. The neck of the retort is connected with a receiver. The mixture on gentle heating on a water bath gives nitrogen pentoxide vapour which condenses to an orange coloured liquid in the receiver. The liquid when cooled in freezing mixture yields colourless crystals of nitrogen pentoxide.

(B) It may also be obtained by passing dry chlorine over dry powdered silver nitrate heated to 60°C.



(C) Nitrogen pentoxide is obtained by the action of ozone on cooled liquid dinitrogen tetroxide.



Properties : Physical—(1) At ordinary temperature, nitrogen pentoxide is a colourless, crystalline solid.

Chemical : (1) At 30°C, it first transforms into an orange coloured liquid which gradually decomposes into brown nitrogen dioxide gas and oxygen. At 50°C, the decomposition takes place with explosion. $2\text{N}_2\text{O}_5 = 4\text{NO}_2 + \text{O}_2$

Comparison of the oxides of nitrogen

N ₂ O	NO	N ₂ O ₃	NO ₂	N ₂ O ₅
Colourless gas with faint pleasant smell, causes hysterical laughter. Does not produce brown fumes with air	Colourless, odourless gas. Reacts with oxygen of the air producing brown fumes $2\text{NO} + \text{O}_2 = 2\text{NO}_2$.	Deep brown, odourless gas. Blue liquid at low temp. Decomposes readily giving brown fumes $\text{N}_2\text{O}_3 \rightleftharpoons \text{NO}_2 + \text{NO}$	Deep brown gas with pungent, suffocating odour, condenses to a yellow liquid at low temp.	Colourless, odourless solid substance. Evolves brown fumes on warming. $2\text{N}_2\text{O}_5 = 4\text{NO}_2 + \text{O}_2$ Acidic oxide.
Neutral oxide Soluble in cold water, insoluble in hot water.	Neutral oxide. Slightly soluble in cold water.	Acidic oxide Dissolves in water giving nitrous acid $\text{N}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{HNO}_2$	Acidic oxide. Dissolves in cold water giving nitrous and nitric acids. With hot water, it forms nitric acid and nitric oxide. $2\text{NO}_2 + \text{H}_2\text{O} = \text{HNO}_2 + \text{HNO}_3$, $3\text{NO}_2 + \text{H}_2\text{O} = 2\text{HNO}_3 + \text{NO}$	Dissolves readily in water giving nitric acid $\text{N}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{HNO}_3$
Not combustible, supports combustion. Decomposes to nitrogen and oxygen on heating. Rekindles a glowing chip of wood. Burning sulphur, carbon, phosphorus, magnesium burn in it brilliantly.	Does not burn, ordinarily does not support combustion. Extinguishes glowing chip of wood. Vigorously burning carbon, sulphur, phosphorus, magnesium continue to burn in the gas.	Does not burn ordinarily, non-supporter of burning, does not rekindle a glowing chip of wood. Burning of carbon, phosphorus, sulphur, magnesium is possible at high temperatures.	Not combustible and ordinarily non supporter of combustion. Vigorously burning carbon, sulphur, phosphorus, sodium, magnesium continue to burn in it.	Being a solid at ordinary temp it is not a supporter of combustion.
Acts as an oxidising agent.	Possesses oxidising properties. It is absorbed by cold ferrous sulphate soln.	Possesses oxidising properties, liberates iodine from potassium iodide.	Possesses oxidising properties, liberates iodine from potassium iodide. It is absorbed by conc. sulphuric acid and alkali solutions.	Possesses oxidising properties.

All the oxides of nitrogen are reduced to nitrogen by heated copper, iron, sodium and potassium.

(2) It is an acidic oxide and a hygroscopic solid. It readily dissolves in water producing nitric acid. Therefore, it is called the anhydride of nitric acid.



The reaction with water takes place vigorously with evolution of much heat.

(3) Feebly burning charcoal burns brilliantly in nitrogen pentoxide vapours. Phosphorus, sodium burn in liquid nitrogen pentoxide if warmed.

(4) It behaves as an oxidising agent. Iodine is oxidised by it to iodine pentoxide (I_2O_5).

Oxides of phosphorus : The chief oxides of phosphorus are .

(1) Phosphorus trioxide— P_2O_3 or $(\text{P}_2\text{H}_5)_2$

(2) Phosphorus pentoxide— P_2O_5 or $(\text{P}_2\text{H}_5)_2\text{O}$

PHOSPHORUS TRIOXIDE [P_2O_3]

Preparation : Phosphorus trioxide is prepared by oxidising white phosphorus at ordinary or slightly elevated temperature in a limited supply of air. $4\text{P} + 3\text{O}_2 = 2\text{P}_2\text{O}_3$

Pieces of white phosphorus are taken in a tube. One end of the tube is connected through a condenser to a U-tube kept immersed in a freezing mixture. A plug of glass wool is inserted in the condenser at the end near to the U-tube. Warm water at 60° is circulated through the outer jacket of the condenser. Slow stream of air is then passed over the pieces of gently heated phosphorus through the other end of the tube when phosphorus burns and is

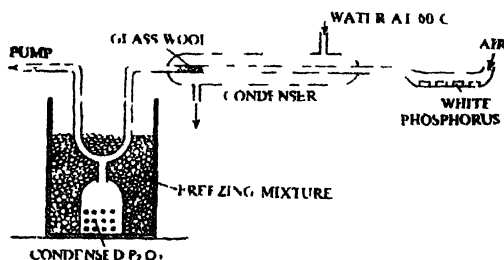


Fig. 2(58) Preparation of phosphorus trioxide

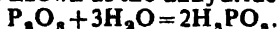
oxidised to phosphorus trioxide. The oxide passes through the condenser in the form of vapour. It condenses to a solid mass in the cooled U-tube. A little phosphorus pentoxide which is also formed remains as floating particles in this condition and is arrested by the glass wool in the condenser. Passing of air through the apparatus is maintained by a suction pump.

Properties: Physical—At ordinary temperature, phosphorus trioxide is a white, wax-like solid (melting point 23.8°C and boiling point 113°C). It has a garlic odour.

It is poisonous. Its vapour density is 110, which shows the correct molecular formula to be P_2O_3 . It is soluble in water and many organic solvents like ether, benzene, carbon disulphide, chloroform etc. but it bursts into flame in contact with alcohol.

Chemical: (1) Phosphorus trioxide is readily oxidised by air or oxygen to phosphorus pentoxide. $\text{P}_2\text{O}_3 + \text{O}_2 = \text{P}_2\text{O}_5$

It burns with a green flame in chlorine or warm oxygen. (2) It is an acidic oxide and reacts with cold water producing phosphorus acid. Hence, it is known as the anhydride of phosphorus acid.



With hot water, it gives phosphine and phosphoric acid.



The reaction takes place with a mild explosion.

PHOSPHORUS PENTOXIDE [P_2O_5]

Preparation: (A) By oxidation of white phosphorus: Phosphorus pentoxide is readily prepared by burning white phosphorus in excess of dry air or oxygen. $4\text{P} + 5\text{O}_2 \rightarrow 2\text{P}_2\text{O}_5$

Pieces of white phosphorus are taken in a crucible and ignited with the help of a heated iron wire. The crucible is covered with a bell-jar when white clouds of pentoxide vapours along with a little phosphorus trioxide are formed. The clouds on cooling settle down in the form of a soft white powder. To complete the oxidation, the bell-jar is lifted from to time for the entry of fresh air to the burning phosphorus.

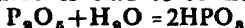
The pentoxide containing the lower trioxide in minute amount is purified by sublimation in a current of dry air (or better ozonised air) over platinised asbestos acting as a catalyst. The trioxide gets oxidised to the pentoxide and the sublimate is collected in a cooled receiver.

(B) By decomposition of ortho phosphoric acid: Ortho phosphoric acid on being heated at a high temperature is dehydrated to give phosphorus pentoxide. When heated to 213°C , orthophosphoric acid is slowly converted into pyro phosphoric acid which in turn is transformed into metaphosphoric acid at 316°C . On continued heating at still higher temperature, metaphosphoric acid yields some phosphorus pentoxide.

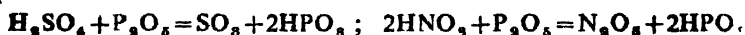


Properties : Physical—Ordinarily, phosphorus pentoxide is a white powder. On cooling, it begins to change into a crystalline solid looking like snow. It sublimes at 250°C . Its vapour density is 142 which corresponds to the molecular formula P_2H_{10} . When kept in dark after a short exposure to light, it begins to glow.

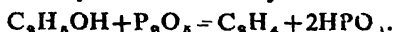
Chemical : It is an acidic oxide. It reacts with cold water with a hissing sound producing metaphosphoric acid. With excess of boiling water, it yields orthophosphoric acid. Metaphosphoric acid formed in the cold is also converted into orthophosphoric acid. Phosphorus pentoxide is said to be the anhydride of orthophosphoric acid.



It has a great affinity for water. It easily absorbs water or water vapour. It can also abstract the elements of water from other compounds. It dehydrates conc. sulphuric and nitric acids giving their anhydrides, the oxide itself being converted into metaphosphoric acid.



It dehydrates ethyl alcohol to ethylene



Uses . (1) As a powerful hygroscopic substance, it is used in desiccators or gas-towers for drying moist solids, liquids or gases. It is a better dehydrating agent than conc. sulphuric acid or anhydrous calcium chloride.

(2) It is also employed in the preparation of phosphoric acid.

Oxides of sulphur : Sulphur has two chief oxides.

Name	Formula	At ordinary temp.	Oxidation No. of S
Sulphur dioxide	SO_2	Gaseous	+4
Sulphur trioxide	SO_3	Solid	+6

Both the oxides are acidic in nature. Other oxides of sulphur are also known.

SULPHUR DIOXIDE [SO_2]

Sulphur dioxide was first prepared by Priestley in 1774 by heating a mixture of mercury and concentrated sulphuric acid,

Preparation : (A) By reducing concentrated sulphuric acid :

Laboratory method : In the laboratory, sulphur dioxide is generally prepared by heating copper turnings with concentrated sulphuric acid. Sulphuric acid is reduced by copper to produce sulphur dioxide. Copper sulphate formed remains in solution.



Copper turnings are taken in a roundbottomed flask fitted with

a thistle funnel and a delivery tube. Concentrated sulphuric acid is then poured through the funnel so that its end and the copper turnings remain under the liquid. The end of the delivery tube is introduced in a bottle containing concentrated sulphuric acid. The bottle is attached with another delivery tube, the end of which is kept in a gas jar. On heating the flask slowly, sulphur dioxide is evolved. It is dried by passing through concentrated sulphuric acid and collected by upward displacement of air. To get the perfectly dry gas, it is collected over mercury.

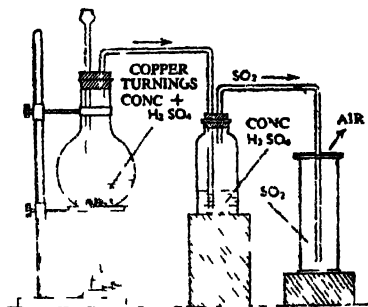
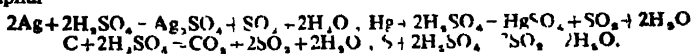


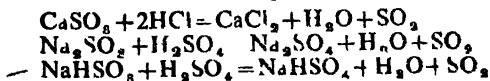
Fig. (59) Preparation of sulphur dioxide in the laboratory

NB. (a) Concentrated sulphuric acid may also be reduced to sulphur dioxide by heating with the metals like silver, mercury and the non-metals like carbon or sulphur



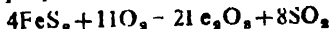
(b) Copper sulphate may be obtained from the liquid left in the flask after the evolution of sulphur dioxide. The liquid is diluted and evaporated when the blue crystals of copper sulphate separate out

(B) From sulphites and bisulphites Sulphur dioxide is evolved when a sulphite or a bisulphite is treated with dilute sulphuric acid or hydrochloric acid at room temperature



(c) Sulphur dioxide may be synthesised by burning sulphur in air or oxygen. $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$

(d) **By roasting mineral sulphides** On a commercial scale, sulphur dioxide is prepared by roasting iron pyrites in air.

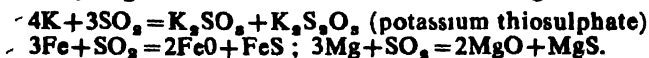


Sulphur dioxide is obtained as a byproduct during roasting of many mineral sulphides.



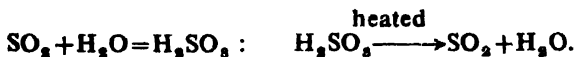
Properties : Physical—(1) Sulphur dioxide is a colourless gas having a suffocating odour of burning sulphur. (2) It is heavier than air. (3) It is highly soluble in water. (4) Dry sulphur dioxide can be liquefied easily to a colourless liquid by the application of pressure (2.5 atm. at 15°C) or by cooling in freezing mixture under ordinary pressure.

Chemical : (1) Sulphur dioxide is *not combustible* and *ordinarily does not support* combustion but burningg sodium, potassium, iron powder, magnesium etc. continue to burn in the gas.

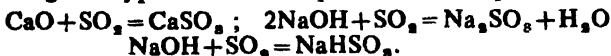


In these reactions, sulphur dioxide behaves like an oxidising agent.

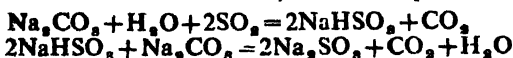
(2) *It is an acidic oxide.* It dissolves in water giving an unstable weak, dibasic acid known as sulphurous acid (H_2SO_3) which turns blue litmus red. Its aqueous solution on being heated expels sulphur dioxide again. It is called the anhydride of sulphurous acid.



It reacts with the basic oxides giving sulphites and with alkalis, yielding two types of salts—sulphites and bisulphites.

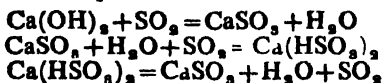


Sulphur dioxide reacts with sodium carbonate solution forming sodium bisulphite with evolution of carbon dioxide. In presence of excess of sodium carbonate, sodium sulphite is formed.



Sulphur dioxide turns clear lime water milky due to the precipitation of insoluble calcium sulphite which forms soluble calcium bisulphite with excess of the gas. Consequently, the milkiness disappears.

The milkiness reappears on boiling the solution as the bisulphite in the solution decomposes to produce insoluble sulphite again with evolution of sulphur dioxide.



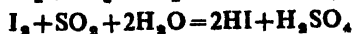
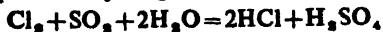
(3) *Sulphur dioxide is oxidised to sulphur trioxide* by oxygen or air at $450^\circ C$ in prescnce of a catalyst like platinum or vanadium pentoxide. This is the main reaction in the contact process of manufacturing sulphuric acid. $2SO_2 + O_2 = 2SO_3$.

This oxidation may also be brought about by nitrogen dioxide acting as a catalyst. Sulphur dioxide is also oxidised by ozone.



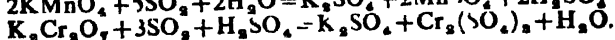
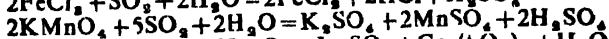
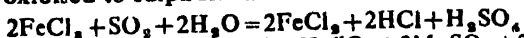
(4) *Sulphur dioxide possesses remarkable reducing properties.* When passed through chlorine or bromine water or water containing suspended iodine, it reduces the halogen to the hydracid, it itself being oxidised to sulphuric acid.

In these cases, the reduction is caused due to the addition of electropositive hydrogen to the halogens.

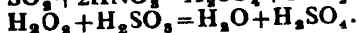
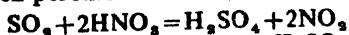


It reduces ferric chloride solution to ferrous chloride, the colour of the solution changes from yellow to colourless or slightly greenish. During reduction, trivalent iron is converted into bivalent iron or the proportion of electro-negative element chlorine is decreased. The pink solution of acidified potassium permanganate on being treated with sulphur dioxide becomes colourless. The gas reduces permanganate to manganous salt when heptavalent manganese (Mn^{VII}) is changed to bivalent manganese (Mn^{II}).

Sulphur dioxide turns orange yellow solution of acidified potassium dichromate green reducing the dichromate to chromic salt. Here, hexavalent chromium (Cr^{VI}) is transformed into trivalent chromium (Cr^{III}). While reducing, sulphur dioxide itself is oxidised to sulphuric acid.



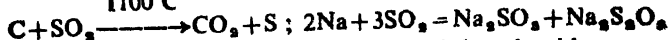
It reduces nitric acid to nitrogen dioxide (brown gas) and hydrogen peroxide to water,



(5) In some cases, sulphur dioxide is found to act as an oxidising agent.

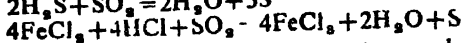
Generally, the gas is a non-supporter of combustion. But burning magnesium, sodium, carbon burn in the gas.

1100°C



These are the examples of oxidation by sulphur dioxide.

It oxidises moist hydrogen sulphide to sulphur. In strongly acid medium, ferrous chloride is oxidised into ferric chloride by sulphur dioxide.



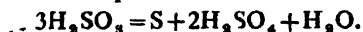
N.B. We find that sulphur dioxide can act as a reducing agent as well as an oxidising agent. It is oxidised to sulphur trioxide by taking up oxygen from other substances. The oxidising action of this gas is due to its ability to accept oxygen. Again, it is converted to elementary sulphur by giving up its oxygen to other substances. In this case, it shows its reducing property. The oxidising

and reducing properties of SO_2 can be easily explained in the light of oxidation number. In SO_2 , the oxidation number of sulphur is +4. The oxide can be oxidised to a compound (SO_3) in which the oxidation number of sulphur +6, and hence can act as a reducing agent. Moreover, sulphur dioxide can be reduced to elementary sulphur with an oxidation number 0. So, due to the decrease of oxidation number from +4 to 0, sulphur dioxide can act as an oxidant.

(6) In some reactions, *sulphur dioxide forms additive compounds* with some elements or compounds.



(7) When a saturated aqueous solution of sulphur dioxide (sulphurous acid) is heated in a sealed tube to 150°C , a yellow solid separates. This yellow solid substance is sulphur. When dry, it dissolves in carbon disulphide and burns in air producing sulphur dioxide which turns a piece of paper soaked in orange yellow solution of acidified potassium dichromate green. This conclusively proves that sulphur dioxide contains sulphur.



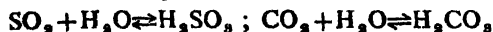
(8) *It is a bleaching agent.* It decolourises many coloured organic matter in presence of water. Perfectly dry gas has no bleaching action on a dry coloured substance. It is probable that sulphur dioxide reacts initially with water producing nascent hydrogen which bleaches the colouring matter.

$\text{SO}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{H}$; coloured substance + 2H = colourless product.

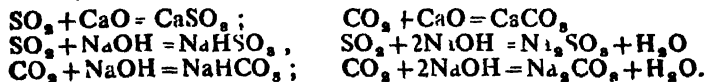
Comparison of the properties of sulphur dioxide and carbon dioxide

Sulphur dioxide and carbon dioxide show marked similarities and dissimilarities in their properties. Both the compounds are colourless gases which can easily be liquefied. They are heavier than air. Carbon dioxide is odourless while sulphur dioxide possesses a suffocating smell of burning sulphur.

Both sulphur dioxide and carbon dioxide are neither combustible nor supporter of combustion. Both are acidic oxides and dissolve readily in water giving unstable, weak sulphurous acid and carbonic acid respectively.



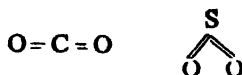
As acidic oxides, they react similarly with basic oxides or alkalis producing salts.



Both the oxides on being reacted with lime water give rise to the similar products. Sulphur dioxide possesses remarkable reducing and bleaching properties whereas carbon dioxide has none of these. Thus, sulphur dioxide turns orange yellow solution of

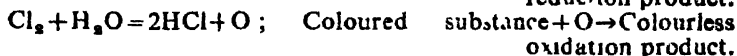
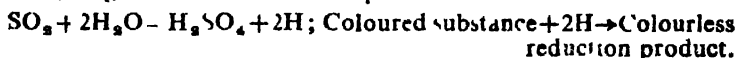
acidified potassium dichromate green as it reduces the dichromate to the green coloured chromic salt. No such reduction can be brought about by carbon dioxide. In CO_2 , carbon is in its highest state of oxidation (+4). Thus, it can act only as an oxidant; it can never behave as a reductant or form an addition product. On the otherhand, the oxidation number of sulphur in SO_2 is +4 it can be increased to +6 or reduced to 0. So, sulphur dioxide can act as both an oxidising and a reducing agents. It tends to form addition compounds.

The molecule of CO_2 is linear while that of SO_2 possesses an angular structure, with the O-S-O angle of about 120°



Comparison between the bleaching properties of sulphur dioxide and chlorine: (a) Both sulphur dioxide and chlorine bleach in presence of moisture. None of the substances when dry is capable of bleaching any dry colouring matter.

(b) Sulphur dioxide acts upon the moisture (water) liberating nascent hydrogen. This reactive hydrogen then reduces the coloured substance with the formation of a colourless product. In the case of bleaching by chlorine, chlorine firstly reacts with water producing nascent oxygen which subsequently oxidises the colouring matter giving rise to the colourless product.



Hence sulphur dioxide bleaches by reduction whereas chlorine by oxidation.

(c) In many cases, the original colour of a substance bleached by sulphur dioxide is restored on exposure to air and light or by the action of cold dilute sulphuric acid. This happens as the decolourised substance gets oxidised to the original substance. But the coloured substance bleached by chlorine can never be brought to its original colour. Thus, decolourisation by sulphur dioxide is not always permanent while bleaching action of chlorine is permanent.

(d) Sulphur dioxide is a milder bleaching agent than chlorine. Delicate articles such as silk, wool etc. are likely to be damaged when bleached by chlorine. Sulphur dioxide, on the other hand, bleaches these substances easily without causing any injury.

Experiments to illustrate the important properties of sulphur dioxide:

(i) *It is noncombustible and ordinarily does not support combustion.* When a lighted taper is introduced in a jar of sulphur dioxide, the taper is extinguished and the gas does not burn.

(ii) *It is highly soluble in water and the aqueous solution is acidic turning blue litmus red.*

Fountain experiment: A roundbottomed flask is fitted with a cork through which passes a long tube ending in a jet inside the flask. The flask is filled with sulphur dioxide and clamped in an inverted position so that the other end of the tube dips in water coloured blue by litmus. The flask is then cooled when the gas contracts and a partial vacuum is created inside. As a result, the blue solution rises up through the tube and enters the flask in the form of a fountain. The blue litmus solution in the flask turns red. This experiment proves simultaneously the solubility of sulphur dioxide in water and the acidic character of its aqueous solution.

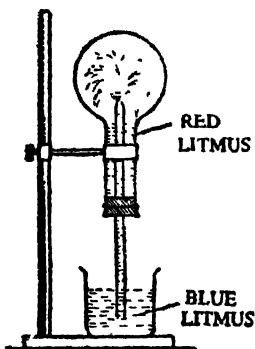


Fig. 2(60) Fountain experiment

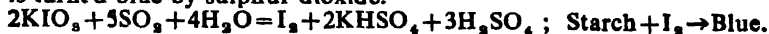
(iii) *It is a powerful reducing agent*
Acidified potassium dichromate solution, acidified potassium permanganate solution, acidified ferric chloride solution and bromine water or water containing suspended iodine are taken separately in four test tubes. Now, sulphur dioxide is passed through each of the tubes and the change of colour is noted in each case. It is seen that the pink potassium permanganate solution has been decolourised, orange yellow solution of potassium dichromate has become green, yellow colour of the ferric chloride solution is discharged or turns slightly greenish and the bromine water has become colourless. All these reactions are good examples to illustrate the reducing action of sulphur dioxide. (The changes involved and the equations have been described under the chemical properties of sulphur dioxide).

(iv) *Sulphur dioxide is a good bleaching agent.* It cannot bleach in absence of water. When some dry coloured flowers are plunged into a gas-jar containing dry sulphur dioxide, flowers are not decolourised. But the flowers when moist are immediately bleached by the gas.

Uses : (1) Sulphur dioxide is mainly used in the manufacture of sulphuric acid and in the preparation of metallic sulphites and bisulphites employed in paper industry. (2) It finds its application as an excellent disinfectant in fumigation and as a germ killer in agriculture. It is used in preserving fruits, meat, wine etc. (3) It is used in bleaching delicate materials like wood, silk, etc. (4) Liquid sulphur dioxide is employed as a refrigerating agent. (5) Sulphur dioxide gas is also used as an *antichlor* to remove excess of chlorine from substances bleached by chlorine.

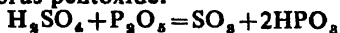
Tests : (1) Sulphur dioxide may be detected by its characteristic suffocating smell of burning sulphur. (2) A piece of paper

soaked in acidified potassium dichromate solution is turned green when held in the gas. (3) The pink colour of the acidified solution of potassium permanganate is discharged by the gas. (4) A piece of paper moistened with a solution of potassium iodate and starch is turned blue by sulphur dioxide.



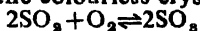
SULPHUR TRIOXIDE [SO_3]

Preparation : (A) **Laboratory method :** In the laboratory, sulphur trioxide is prepared by dehydrating concentrated sulphuric acid by phosphorus pentoxide.



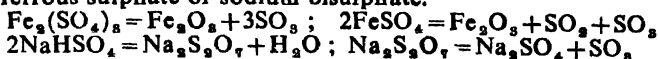
On distillation of a mixture of concentrated sulphuric acid and phosphorus pentoxide in a retort, sulphur trioxide collects as a distillate and metaphosphoric acid formed remains in the retort.

(B) Sulphur dioxide is not easily oxidised to sulphur trioxide by the action of oxygen. But when a mixture of sulphur dioxide and excess of oxygen (air) is passed over platinised asbestos or vanadium pentoxide (catalyst) heated to 450°C , fumes of sulphur trioxide are evolved. The fumes on cooling in a receiver kept immersed in a freezing mixture form the colourless crystals of sulphur trioxide.



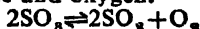
In fact, this is the main reaction in the manufacture of sulphuric acid by the contact process.

(C) It can also be obtained by heating anhydrous ferric sulphate, ferrous sulphate or sodium bisulphate.

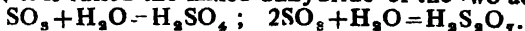


Properties : **Physical**—At ordinary temperature, sulphur trioxide is a colourless, silky, crystalline solid.

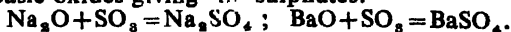
Chemical : (1) When passed through a red hot tube, it breaks up into sulphur dioxide and oxygen.



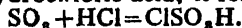
(2) Sulphur trioxide is an acidic oxide and a strong hygroscopic substance. It fumes in the moist air and reacts vigorously with cold water producing sulphuric acid and pyrosulphuric acid. This is why, it is called the mixed anhydride of the two acids.



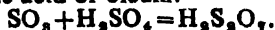
The reaction with water takes place with a hissing sound and with evolution of great amount of heat. The oxide directly unites with some basic oxides giving the sulphates.



(3) With hydrochloric acid, it forms chlorosulphonic acid.



(4) It dissolves in 98% sulphuric acid producing sulphuric acid but the major part forms pyrosulphuric acid. This is called fuming sulphuric acid or oleum.



CHAPTER 5

OXY-ACIDS

NITROUS ACID [HNO_2]

Nitrous acid is a very unstable compound. It can never be obtained in the pure state. The free acid is only known in solution but its salts, the nitrites, are however stable, crystalline compounds.

Preparation : (A) When ice-cold barium nitrite solution is treated with theoretical quantity of cold dilute sulphuric acid, nitrous acid and barium sulphate are formed by double decomposition. $\text{Ba}(\text{NO}_2)_2 + \text{H}_2\text{SO}_4 = \text{BaSO}_4 + 2\text{HNO}_2$

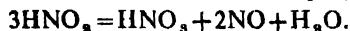
The precipitated barium sulphate is filtered off and the resulting filtrate is an aqueous solution of nitrous acid.

(B) Nitrous acid can also be obtained by treating well-cooled aqueous solution of other nitrites with dilute hydrochloric or sulphuric acid. $\text{NaNO}_2 + \text{HCl} = \text{NaCl} + \text{HNO}_2$

(C) The aqueous solution of the acid is also obtained by the action of nitrogen trioxide on water at 0°C .



Properties : (1) Nitrous acid is an unstable, weak, monobasic acid. Its aqueous solution is pale blue in colour. The acid decomposes to nitric acid and nitric oxide on keeping or heating.

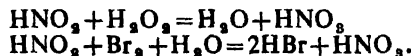


At higher temperatures, nitrogen peroxide and nitric oxide are evolved. $2\text{HNO}_2 \rightleftharpoons \text{NO}_2 + \text{NO} + \text{H}_2\text{O}$

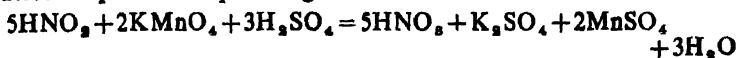
The salts of the acid are known as nitrites such as potassium nitrite KNO_2 , silver nitrite AgNO_2 etc. Metallic copper or silver dissolves slowly in the solution of the acid.



(2) Nitrous acid is a reactive substance. It possesses both oxidising and reducing properties. Thus, it reduces hydrogen peroxide to water, chlorine and bromine to their hydric acids.

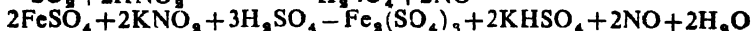
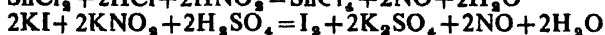
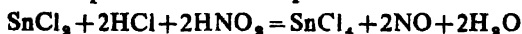


Bromine water becomes colourless. It decolourises the violet colour of an acidified solution of potassium permanganate as the acid reduces the permanganate in acid to manganous salt. Alkaline solution of potassium permanganate has no action on nitrous acid.



In each of the above reactions, nitrous acid itself is oxidised to nitric acid.

(3) The oxidising properties of nitrous acid are very remarkable. It oxidises stannous chloride to stannic chloride, acidified potassium iodide to iodine, sulphur dioxide to sulphuric acid and acidified ferrous sulphate to ferric sulphate.

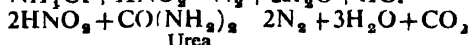


Hydrogen sulphide is oxidised to sulphur when passed through a solution of nitrous acid. $\text{H}_2\text{S} + 2\text{HNO}_2 = \text{S} + 2\text{NO} + 2\text{H}_2\text{O}$.

In each of the reactions just mentioned, nitrous acid itself is reduced to nitric oxide.

Nitrous acid can act as a reducing agent because it is capable of being oxidised to nitric acid by taking an oxygen atom from other substances. On the other hand it acts as an oxidising agent because it is easily reduced to nitric oxide.

(4) Nitrous acid reacts with ammonia, ammonium salts or an organic compound containing amino ($-\text{NH}_2$) group liberating nitrogen



Uses It is mainly used for the detection of $-\text{NH}_2$ group in the organic compounds. It is also employed in the organic syntheses.

Tests for nitrous acid and nitrites (1) An aqueous solution of nitrous acid or a nitrite yields reddish brown fumes of nitrogen dioxide on acidification with dilute sulphuric acid.

(2) Nitrous acid or a nitrite solution liberates iodine from an acidified solution of potassium iodide. The liberated iodine turns starch solution intense blue.

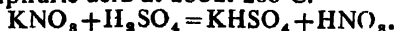
(3) The acidified potassium permanganate solution is decolourised by nitrous acid or a nitrite solution.

(4) A solution of meta phenylene diamine is coloured brown when acted upon by nitrous acid or a nitrite solution.

NITRIC ACID [HNO_3]

The uses of nitric acid were known to the alchemists. They called it aqua fortis. It was first obtained by Glauber (1648) by distilling nitre (KNO_3) with sulphuric acid.

Preparation : Laboratory method—In the laboratory, nitric acid is prepared by heating potassium nitrate (or sodium nitrate) with concentrated sulphuric acid at about 200°C .



Equal parts by weight of potassium nitrate (or sodium nitrate) and concentrated sulphuric acid are taken in a stoppered glass

retort, the neck of which is introduced into a roundbottomed flask (receiver) floating on and kept cooled by water. The retort is then kept on a wire gauze and clamped to a stand as in Fig. 2(61). On heating the mixture in the retort slowly to about 200°C, nitric acid vapour evolves and collects in the watercooled receiver as a yellowish liquid.

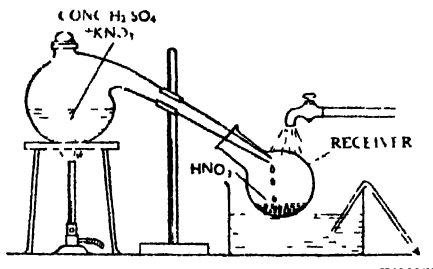


Fig. 2(61) Preparation of nitric acid in the laboratory

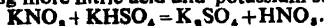
The acid thus obtained is not pure.

It has a yellow colour owing to the presence of some dissolved nitrogen dioxide resulting from the decomposition of the acid.



The acid containing water and nitrogen dioxide as impurities is distilled at low pressure with concentrated sulphuric acid when 98% nitric acid is obtained. The oxide of nitrogen is removed by bubbling air or carbon dioxide at 70°C through the acid till it becomes colourless. Pure nitric acid completely free from water may be obtained as colourless crystals by freezing the 98 percent acid at -42°C.

N.B. (1) Concentrated sulphuric acid is not a volatile acid and is conveniently used to expel the volatile nitric acid from a nitrate. Hydrochloric acid, on the other hand, is a volatile acid, even more volatile than nitric acid. If hydrochloric acid is used to decompose a nitrate, the acid will invariably distil along with the nitric acid vapour and collects in the receiver. This is why hydrochloric acid is unsuitable for the preparation of nitric acid by the above method. (2) If the mixture of potassium nitrate and concentrated sulphuric acid is heated above 200°C, the reaction between the potassium bisulphate and potassium nitrate takes place (at about 800°C) producing more nitric acid and potassium sulphate.



But this reaction at the higher temperature is not allowed to take place for some reasons. Firstly, at the high temperature necessary to effect the reaction, a considerable amount of nitric acid decomposes into nitrogen dioxide, oxygen and steam. Secondly, the product potassium bisulphate resulting from the first reaction remains in molten state and is easily removed from the retort. But the potassium sulphate obtained as a product of the second reaction remains in the solid state and cannot be easily removed. Moreover, nitric acid vapour at higher temperatures attacks the materials of which the retort is made.

Properties : Physical—(1) Pure nitric acid is a colourless, fuming liquid of specific gravity 1.52 at 15°C. (2) It boils at 86°C and freezes at -42°C into a transparent crystalline substance. (3) It is highly soluble in water.

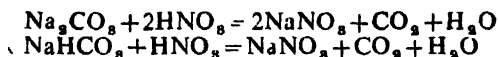
Chemical : (1) **Action of heat** : Nitric acid is readily decomposed by heat yielding oxygen, steam and brown vapours of nitrogen dioxide. $4\text{HNO}_3 = 4\text{NO}_2 + \text{O}_2 + 2\text{H}_2\text{O}.$

This decomposition also takes place slowly even in sunlight. This is why concentrated acid turns yellow in sunlight.

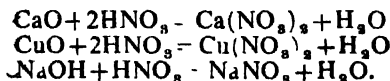
Nitric acid exhibits three different modes of chemical behaviour :

It acts (a) as an acid, (b) an oxidising agent and (c) a nitrating agent.

(2) **Acidic properties of nitric acid :** It is a strong monobasic acid. It possesses all the general characteristics of an acid in aqueous solution. It ionises almost completely to nitrate and hydrogen (hydroxonium) ions. $\text{HNO}_3 \rightleftharpoons \text{H}^+ + \text{NO}_3^-$. It turns blue litmus solution red and liberates carbon dioxide from a carbonate or a bicarbonate.



It reacts with basic oxides and hydroxides giving salts and water.



Magnesium and manganese displace hydrogen from very dilute nitric acid and dissolve in the latter producing the metallic nitrates.

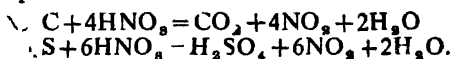


Other metals standing above hydrogen in the electro chemical series fail to liberate molecular hydrogen as the nascent hydrogen initially formed is oxidised to water by the oxidising action of the acid.

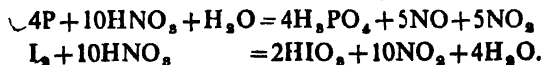
Being a mono basic acid, it gives rise to normal salts only. All nitrates are soluble in water excepting bismuth oxynitrate, BiONO_3 .

(3) **Oxidising properties of nitric acid :** Nitric acid is a powerful oxidising agent. The acid, particularly when hot and concentrated, liberates nascent oxygen which oxidises the metals, non-metals and various compounds. The acid itself is reduced to oxides of nitrogen.

(a) When heated with concentrated nitric acid, most non-metals are oxidised to their oxides or highest oxy-acids. Nitric acid itself is reduced to nitrogen dioxide or nitric oxide. Thus, hot and concentrated nitric acid oxidises carbon to carbon dioxide, sulphur to sulphuric acid.



Phosphorus and iodine are oxidised to phosphoric acid and iodic acid respectively by the action of hot, concentrated nitric acid which is as usual reduced to nitrogen oxides.

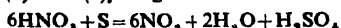


Oxygen, nitrogen, chlorine and bromine are not attacked by nitric acid.

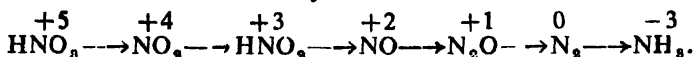
The equations of the oxidation reactions may be represented by the partial equations. The oxidation of sulphur is as follows—



On adding (1), (2) and (3), we get



(b) The oxidising action of nitric acid on metals is very important. Most metals except gold, platinum, iridium etc. are oxidised by nitric acid to their nitrates or oxides. While oxidising, the acid is reduced successively as follows :

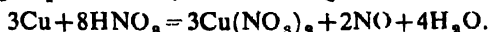


The nature of reduction product will depend on the concentration of the acid, temperature, activity of the metals and the concentration of the products formed. Generally, the metals (except magnesium and manganese) do not displace hydrogen from nitric acid. Certain metals like iron, chromium etc. are rendered 'passive' or protected by oxide films in concentrated acid. The reactions of some metals with nitric acid are shown below.

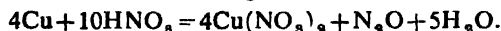
Reactions with copper : (i) Hot and concentrated nitric acid attacks copper giving cupric nitrate (blue solution), nitrogen dioxide (brown) gas and water.



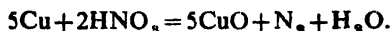
(ii) Cold nitric acid of moderate strength (1 : 1) acts on copper yielding cupric nitrate, nitric oxide gas and water.



(iii) Cold and very dilute acid reacts with copper producing cupric nitrate, nitrous oxide gas and water.



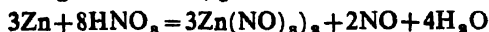
(iv) The reaction between heated copper and vapours of nitric acid produces cupric oxide (black), gaseous nitrogen and steam.



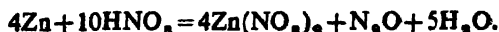
Reactions with zinc : (i) Zinc, with hot and concentrated nitric acid, gives zinc nitrate (colourless solution), brown nitrogen dioxide gas and water.



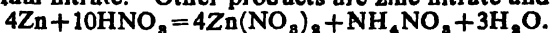
(ii) Cold and moderately concentrated nitric acid (1 : 1) reacts with zinc yielding zinc nitrate, gaseous nitric oxide and water.



(iii) With cold and dilute nitric acid, zinc gives zinc nitrate, nitrous oxide and water.



(iv) Cold and very dilute nitric acid is reduced to ammonia which combines with the excess of the acid present to form ammonium nitrate. Other products are zinc nitrate and water.

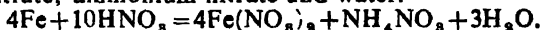


\ *Reactions with iron* : (i) Iron does not react with concentrated or fuming nitric acid. The metal is rendered passive by such acid.

(ii) With hot and concentrated acid, iron gives ferric nitrate, nitrogen dioxide and water.



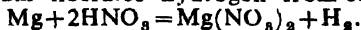
(iii) Cold and dilute nitric acid reacts with iron producing ferrous nitrate, ammonium nitrate and water.



\ *Reactions with magnesium* : (i) Magnesium on being reacted with cold and moderately concentrated nitric acid yields magnesium nitrate, nitric oxide and water.



(ii) Magnesium liberates hydrogen from cold and very dilute nitric acid.



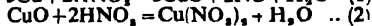
Dilute nitric acid on being reacted with impure aluminium produces aluminium nitrate. Aluminium is not attacked by concentrated nitric acid. It is probable that a part of the metal is first oxidised to aluminium oxide which forms a protective layer on the metal and prevents further reaction. This is why concentrated nitric acid can be kept in aluminium vessels.

The reactions of nitric acid with other metals will be discussed in part II of this book.

It is clear that the mode of reaction between nitric acid and metals is not a simple process. In its action, nitric acid plays a double role. It simultaneously acts as an acid and an oxidising agent. While oxidising, the acid is itself reduced to the oxides of nitrogen and even to ammonia.

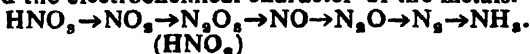
Different theories have been put forward to explain the action of nitric acid on the metals.

(a) *Oxidation theory* : The metals like copper, silver, mercury which stand below hydrogen in the electrochemical series are unable to displace hydrogen from nitric acid. These metals are first oxidised to their oxides which dissolve in excess of the acid producing the respective nitrates. Nitric acid, at the same time undergoes reduction to nitric oxide.

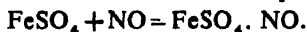


Strong nitric acid when used converts nitric oxide into nitrogen dioxide by oxidation, $2\text{HNO}_3 + \text{NO} = 3\text{NO}_2 + \text{H}_2\text{O}$

(b) *Nascent hydrogen theory* : According to this theory, the metals like zinc, iron etc. which are above hydrogen in the electrochemical series initially attack the acid liberating nascent hydrogen which then reduces the excess of nitric acid to various oxides of nitrogen or to ammonia. Different reduction products are formed under different conditions and according to the strengths of the acid and the electrochemical character of the metals.



The nitric oxide evolved may combine with unreacted ferrous sulphate giving the nitroso additive compound

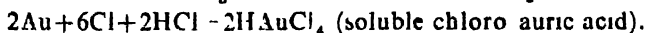
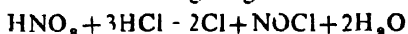


(A mixture consisting of one volume of concentrated nitric acid and three volumes of concentrated hydrochloric acid is called *aqua regia*.

It dissolves the noble metals such as gold and platinum which are not attacked by concentrated nitric acid or concentrated hydrochloric acid alone.

In fact, nitric acid oxidises hydrochloric acid to chlorine. Nitrosyl chloride and water are also formed as the products.

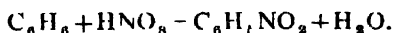
The two acids on being reacted together set free nascent chlorine which combines with the metals giving the soluble chlorides.



(d) Many organic substances are readily oxidised by nitric acid. Turpentine, saw dust, sugar, alcohol etc., when added to conc. nitric acid, are found to burst into flames. It produces painful wounds when it comes in contact with the skin. Skin, feather, silk, leather etc. are stained yellow or brown by strong nitric acid.

Nitric acid also acts as a nitrating agent. It reacts with many organic substances substituting one or more hydrogen atoms in the molecule by nitro groups (NO_2).

This process of substitution of hydrogen atoms by nitro groups is known as nitration. Thus, benzene on being treated with a mixture of concentrated nitric acid and sulphuric acid yields nitro benzene. Sulphuric acid absorbs the water formed.

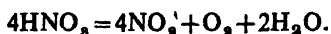


Concentrated nitric acid. Dilute nitric acid on distillation produces 68% nitric acid having a sp. gr. of 1.414. This acid is sold in the market as the concentrated nitric acid. When conc. nitric acid mixed with conc. sulphuric acid is distilled, we get 98% nitric acid.

(**Fuming nitric acid.** Nitrogen dioxide is readily soluble in nitric acid. The brown coloured nitric acid containing dissolved NO_2 (and some N_2O_5) is known as fuming nitric acid. It fumes spontaneously and is a powerful oxidising agent. Fuming nitric acid is obtained by distilling a mixture of concentrated nitric acid and starch or arsenious oxide.

Experiments illustrating some of the properties of nitric acid :

(1) *It decomposes at high temperature giving nitrogen dioxide, oxygen and steam.*

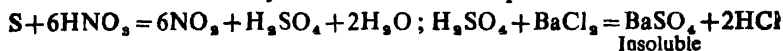


Concentrated nitric acid is dropped on strongly heated pumice stone taken in a round bottomed distilling flask. The gaseous products (coloured brown) evolving through the side tube are allowed to pass successively through two U-tubes, the first one being kept immersed in cold water and the second in freezing mixture. The second U-tube is connected with a delivery tube. Two different liquids are found to collect in the two U-tubes and a gas which comes out of the delivery tube is collected over water.

A glowing chip of wood is rekindled in the gas. That the gas is oxygen is further proved by the fact that it is absorbed by alkaline potassium pyrogallate solution. This experiment conclusively proves that nitric acid contains oxygen.

The colourless liquid collected in the first U-tube is water as it turns anhydrous copper sulphate blue. In the second U-tube, nitrogen dioxide condenses as a brown liquid. The liquid on slight warming gives off brown vapours of nitrogen dioxide which can be detected by its characteristic colour and pungent smell.

(2) *Nitric acid is a powerful oxidising agent.* Conc. nitric acid oxidises sulphur into sulphuric acid. A mixture of powdered sulphur and concentrated nitric acid is heated in a test tube when brown fumes are found to evolve. Soon after the evolution of fumes ceases, the liquid in the tube is cooled, diluted and filtered. On adding a few drops of barium chloride solution to the filtrate, a white precipitate insoluble in hydrochloric acid is obtained. This experiment proves the existence of sulphuric acid which is formed in the filtrate by the oxidation of sulphur.

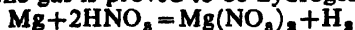


To prove that nitric acid contains hydrogen, nitrogen and oxygen.

Oxygen : The presence of oxygen has been proved by the first experiment illustrating the thermal decomposition of the acid.

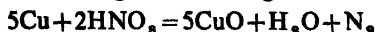
Hydrogen : A piece of magnesium is added to distilled water taken in a Woulfe's bottle. There is no evolution of any gas. On adding a few drops of dilute nitric acid to the content of the bottle, a colourless gas is evolved with effervescence. The gas is collected over water as usual. When a lighted taper is held in the gas, the taper is extinguished but the gas burns with a blue flame.

Hence, the gas is proved to be hydrogen.



Nitrogen : Nitrogen is obtained when nitric acid vapour is passed through a hard glass tube containing red hot copper filings.

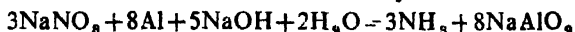
The gas is collected over water and is proved to be nitrogen by its usual tests. It is a colourless, odourless, inert gas which extinguishes a lighted taper. It is absorbed by heated magnesium and the product on heating with water gives off ammonia.



Uses. (1) Nitric acid is widely used in the manufacture of explosives like nitroglycerine, T.N.T., picric acid, gun cotton etc. (2) It is used in the large scale production of artificial silk, dyes, sulphuric acid, celluloids and nitrogenous fertilisers. (3) It is employed in the laboratory as an oxidant, a nitrating agent and an important reagent in many chemical processes (4) Many useful nitrates and aqua regia are prepared from this acid. (5) It is used in dissolving many metals and alloys and for cleaning metals before electro-plating.

Tests for nitric acid and nitrates : When nitric acid or a nitrate is heated with concentrated sulphuric acid and copper turnings, reddish brown fumes of nitrogen dioxide are evolved.

(2) A concentrated solution of a nitrate on being heated with aluminium and strong caustic soda solution gives off ammonia which can be identified by its characteristic pungent smell or by formation of white fumes in contact with hydrochloric acid.



(3) **Ring test :** It is a very useful test for detecting nitric acid or a nitrate radical.

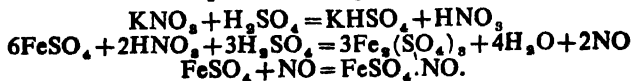
An equal volume of freshly prepared solution of ferrous sulphate is added to a dilute solution of nitric acid or a nitrate (say KNO_3) in a test tube and the mixed solution is cooled.

Concentrated sulphuric acid is then poured slowly and carefully into the liquid (without disturbing it), when the sulphuric acid forms a heavy layer at the bottom and a brown ring is formed at the junction of the two liquids.



Fig. 2(62) Ring Test

In this test, free nitric acid or the nitric acid produced by the action of sulphuric acid on a nitrate is reduced by ferrous sulphate to nitric oxide. This oxide with excess of ferrous sulphate forms the brown additive compound $\text{FeSO}_4 \cdot \text{NO}$.



Brucine Test : When a nitrate (or nitric acid) is added to a

solution of brucine in pure sulphuric acid taken in a porcelain basin, a beautiful red colour is produced.

Distinction between nitrites and nitrates :

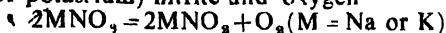
Expt.	Nitrite (NO_2)	Nitrate (NO_3)
(1) Dilute hydrochloric acid is added.	Brown fumes evolved.	No brown fumes.
(2) Acetic acid, potassium iodide and starch solution are added.	Blue colour produced.	No blue colour.
(3) Dilute solution of potassium permanganate acidified with dil. H_2SO_4 is added.	Pink colour discharged.	The solution is not decolourised.
(4) Brucine in conc. H_2SO_4 is added.	No red colour.	Bright red colour produced.
(5) Ring test.	Whole solution turns brown.	Brown ring is formed only at the junction of the acid and the solution.
(6) Urea and dil. H_2SO_4 added.	Effervescence of nitrogen.	Nitrogen is not evolved.

A nitrate containing a little nitrite is first heated with ammonium chloride or urea and sulphuric acid to remove the nitrite as nitrogen. Then, the ring test is applied for detection of the nitrate radical.

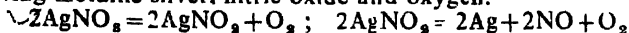
Action of heat on metallic nitrates

All nitrates decompose on heating. But different nitrates give rise to different products on decomposition.

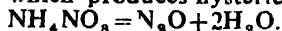
Sodium or potassium nitrate on being strongly heated gives sodium (or potassium) nitrite and oxygen



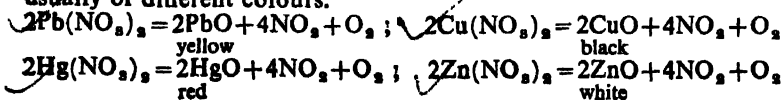
When heated to 450 C, *silver nitrate* decomposes to produce silver nitrite and oxygen. Heated still further, silver nitrite breaks up giving metallic silver, nitric oxide and oxygen.



Ammonium nitrate on gentle heating decomposes giving nitrous oxide, a gas which produces hysteric laughter on inhalation, and water.

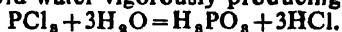


Nitrates of heavy metals like lead, copper etc. undergo thermal decomposition forming the oxides of the metals, brown nitrogen dioxide gas and frequently oxygen. The oxides formed are usually of different colours.



PHOSPHORUS ACID [H_3PO_3]

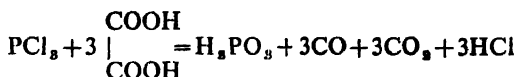
Preparation : (A) Phosphorus trichloride undergoes hydrolysis with cold water vigorously producing phosphorus acid.



The aqueous solution is evaporated to 180°C and cooled, when crystals of phosphorus acid are obtained with the evolution of hydrogen chloride.

(B) It may be obtained by dissolving phosphorus trioxide in cold water. $\text{P}_2\text{O}_3 + 3\text{H}_2\text{O} = 2\text{H}_3\text{PO}_3$.

(c) Phosphorus acid is also prepared by heating a mixture of phosphorus trichloride and oxalic acid.



Properties : Physical— Ordinarily, it is a deliquescent crystalline solid (m.p. 74°C).

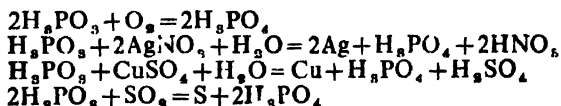
Chemical :—(1) When heated to 200°C , phosphorus acid decomposes into phosphine and phosphoric acid.



(2) It is a dibasic acid. Although the molecule of the acid contains three hydrogen atoms, only two of them are replaceable by metals. The salts are represented by Na_2HPO_3 and NaH_2PO_3 .

(3) It has strong reducing properties. It is slowly oxidised by air to phosphoric acid and precipitates metallic silver from silver nitrate solution or copper from copper sulphate solution. Sulphur dioxide is reduced to sulphur by the acid.

In each case, phosphorus acid itself is oxidised to phosphoric acid.

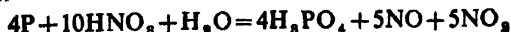
**ORTHO PHOSPHORIC ACID [H_3PO_4]**

This acid is commonly called phosphoric acid.

Preparation : (A) Phosphoric acid is obtained by cautiously adding phosphorus pentoxide to boiling water.

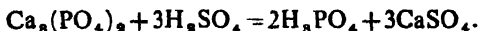


(B) In the laboratory, the pure acid is prepared by heating red phosphorus with concentrated nitric acid. The reaction is accelerated in presence of a crystal of iodine which acts as a catalyst.



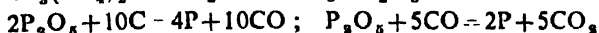
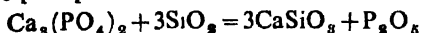
The resulting solution is evaporated to a syrup at 180°C. On cooling the syrup over concentrated sulphuric acid in a vacuum desiccator kept immersed in an ice-salt bath, colourless deliquescent crystals of phosphoric acid separate out.

(C) On a commercial scale, the acid is prepared by digesting bone ash or a mineral phosphate (calcium phosphate) with 60% sulphuric acid.



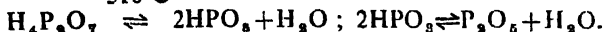
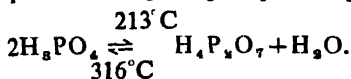
The reaction is brought about in a lead-lined iron tank, heating being done by means of steam. The insoluble calcium sulphate is removed by filtration through a bed of powdered coke and the filtrate is evaporated to a syrup.

(D) Phosphoric acid is also manufactured by heating a mixture of a mineral phosphate, coke and silica in an electric furnace. The phosphorus vapour and carbon monoxide leaving the furnace are mixed with a current of air whereby phosphorus is oxidised to phosphorus pentoxide and carbon monoxide to carbon dioxide. On spraying water on the cooled gas mixture, 85% phosphoric acid is obtained.



Properties : *Physical*—Pure phosphoric acid is a colourless, crystalline solid melting at 42°C. It is highly soluble in water.

Chemical : (1) When heated to 213°C, phosphoric acid loses elements of water and is slowly converted into pyrophosphoric acid which at 316°C forms metaphosphoric acid. Heated still further, metaphosphoric acid gives phosphorus pentoxide.



All the changes are reversible. When orthophosphoric acid is heated and subsequently cooled, it forms a glass-like mass called glacial phosphoric acid.

(2) It is a tribasic acid. Hence, it gives rise to three types of salts, e.g.,

(a) NaH_2PO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$, etc. formed by the replacement of one hydrogen atom. These salts are called primary phosphates or acid phosphates whose aqueous solutions are acidic.

(b) Na_2HPO_4 , CaHPO_4 , etc. formed by the replacement of two hydrogen atoms. These are secondary phosphates, the aqueous solutions of which are almost neutral.

(c) Na_3PO_4 , $\text{Ca}_3(\text{PO}_4)_2$, etc. formed by the replacement of three hydrogen atoms. These salts are designated as the tertiary

phosphates and their aqueous solutions are alkaline to litmus due to hydrolysis.

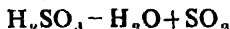
Uses : (1) Syrupy phosphoric acid is widely used as a dehydrating agent. (2) The acid is used in place of concentrated sulphuric acid, where the use of the latter leads to complications. (3) It is employed in the manufacture of sodium, potassium and ammonium phosphates. (4) It is also applied in medicine.

SULPHUROUS ACID [H_2SO_3]

Sulphurous acid is an unstable acid. It has never been isolated in the pure form and is known only in aqueous solution. The salts of the acid are stable crystalline compounds.

Preparation : Sulphurous acid is obtained by dissolving sulphur dioxide in water. $\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_3$.

Properties : It is an unstable, weak dibasic acid. Its aqueous solution on being slightly heated gives off sulphur dioxide.



When an aqueous solution of sulphurous acid is heated to 150°C in a sealed tube, the acid is converted into sulphuric acid with the separation of elementary sulphur.



As a dibasic acid, it gives rise to two types of salts namely bisulphites and sulphites.

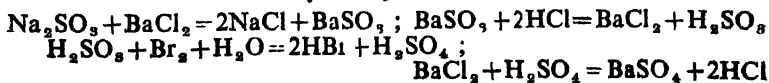


All normal sulphites (except alkali sulphites) are insoluble in water. The aqueous solution of the acid shows powerful reducing properties like sulphur dioxide.

Tests for the sulphite radical (SO_3).

Dry Test : (a) When a solid sample of a sulphite is treated with dilute sulphuric or hydrochloric acid, sulphur dioxide possessing the suffocating odour of burning sulphur is evolved. The gas turns a piece of paper soaked in acidified potassium dichromate solution green.

Wet test : When barium chloride solution is added to a solution of a sulphite, we get a white precipitate of barium sulphite soluble in hydrochloric acid. The resulting clear solution on being slightly warmed with bromine water gives the white precipitate of barium sulphate. The insoluble sulphate is formed due to the oxidation of the sulphite by bromine water.



SULPHURIC ACID [H₂SO₄]

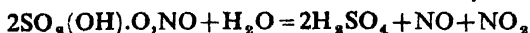
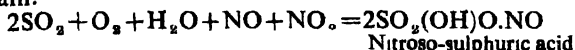
Because of its diverse applications in industries, sulphuric acid is regarded as the most important of all acids. It does not occur free in nature.

Preparation : Sulphuric acid may be obtained by absorbing sulphur trioxide in water or by oxidising aqueous solution of sulphur dioxide by air, chlorine or nitric acid. But the amount of acid produced is so small that these methods have no practical value.

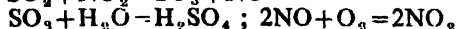
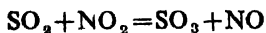
Laboratory method :

Principle : Sulphur dioxide, oxygen (air), water or steam react together under the catalytic influence of gaseous oxides of nitrogen (NO₂, NO) to produce sulphuric acid. In fact, sulphur dioxide is oxidised to sulphur trioxide which subsequently reacts with water to give sulphuric acid.

Many theories have been suggested to explain the mechanism of the formation of sulphuric acid. According to one of them, an intermediate compound nitroso-sulphuric acid is first formed by the interaction of sulphur dioxide, oxygen, oxides of nitrogen and water; the intermediate product is then rapidly decomposed by excess of water with the formation of sulphuric acid and regeneration of the oxides of the nitrogen, which take part in the process again.



An alternative theory suggests that nitrogen dioxide oxidises sulphur dioxide into sulphur trioxide and it itself is reduced to nitric oxide. Sulphur trioxide formed reacts with water to produce sulphuric acid. Nitric oxide is reoxidised by oxygen of the air to nitrogen dioxide which oxidises further quantity of sulphur dioxide.



Here, nitric oxide takes up oxygen from the air and gives it to sulphur dioxide. The cycle of reactions goes on with nitric oxide actually serving as an oxygen-carrier.

Description : A large hard glass flask is fitted with a rubber stopper through which pass five glass tubes. Four of the tubes reach almost near the bottom of the flask and act as the inlet tubes and the fifth one is a short exit tube reaching just below the cork.

The following gaseous substances are introduced into the flask through the four inlet tubes : (i) air, (ii) nitric oxide generated by the action of copper on moderately concentrated nitric acid (iii) sulphur dioxide obtained by heating copper with concentrated sulphuric acid and, (iv) excess of steam produced by boiling water. Before introducing, the gaseous substances are dried by bubbling through concentrated sulphuric acid. (Arrangements for drying have not been shown in the fig.)

Dry air and nitric oxide are first made to enter into the flask when they interact to produce nitrogen dioxide. Sulphur dioxide and steam are then passed successively. Nitroso-sulphuric acid formed as an intermediate compound is hydrolysed by steam to

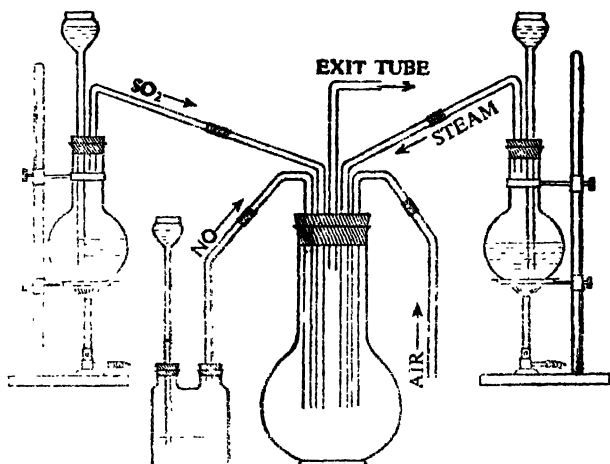


Fig. 2(63) Preparation of sulphuric acid in the laboratory

produce sulphuric acid which collects as an oily liquid in the flask. The remaining gas above the liquid is slightly brown in colour. Excess of air or other unreacted gases escape through the short exit tube.

N.B. If the supply of steam is not sufficient or stopped for some time, instead of the oily acid, white crystals are found to be deposited on the inner walls of the flask. These crystals are known as chamber-crystals (nitroso-sulphuric acid).

Sulphuric acid is generally not prepared in the laboratory. But the manufacture of sulphuric acid by Lead Chamber Process is based on the similar reactions discussed under the laboratory method of preparation.

Properties : Physical—(1) Pure sulphuric acid is a colourless, odourless liquid of oily consistency. (2) It is heavier than water (its density is 1.848 at 15°C). (3) The boiling point of sulphuric acid (98%) is 338°C. (4) It is miscible with water in all proportions. A considerable amount of heat is evolved when the acid dissolves in water. Its aqueous solution is a good conductor of electricity.

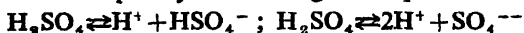
Dilution of sulphuric acid is an exothermic process. When water is added to the concentrated acid, the evolved heat changes some water into steam suddenly causing the acid to spurt dangerously in all directions. When sulphuric acid is added to water, the acid being heavier than water sinks and the heat produced is dissipated through the mass of water. So, in preparing dilute sulphuric acid, the concentrated acid must always be added in a fine stream into cold water with continuous stirring with a glass rod.

Chemical : (1) *Sulphuric acid decomposes when heated strongly forming sulphur dioxide, oxygen and steam.*



(2) *It is a strong dibasic acid in aqueous solution. It possesses properties common to all acids.*

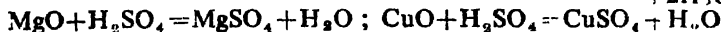
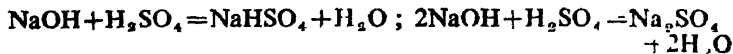
It ionises completely in two stages in aqueous solution.



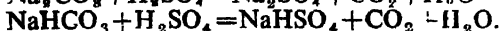
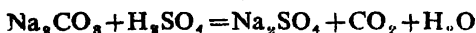
As ionisation increases with dilution, the dilute sulphuric acid is stronger than the concentrated acid.

The acid turns blue litmus red and reacts with bases or alkalis to produce salts and water. As a dibasic acid, it forms normal salts and acid salts such as Na_2SO_4 , NaHSO_4 etc.

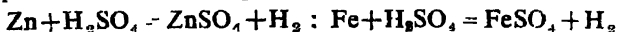
All the sulphates except lead, barium and strontium sulphates are soluble in water. Calcium sulphate is slightly soluble in water.



At ordinary temperature, it liberates carbon dioxide from carbonates and bicarbonates,



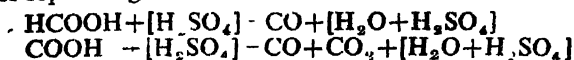
Metals like zinc, magnesium, iron etc. standing over hydrogen in the electro chemical series liberate hydrogen from cold, dilute sulphuric acid. The sulphates of the metals are also formed



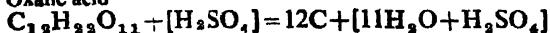
(3) *The pure acid has a strong affinity for water. Due to this affinity, it is used to dry moist air or gases. Sulphuric acid mixes with water at low temperatures forming crystalline hydrates such as $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ etc.*

Concentrated sulphuric acid abstracts the elements of water from many organic compounds. Thus when a mixture of formic acid and concentrated sulphuric acid is heated, carbon monoxide is produced. With hot and concentrated sulphuric acid, oxalic acid is dehydrated to give carbon monoxide and carbon dioxide.

Concentrated sulphuric acid chars starch, sugar etc. In other words, the acid takes up the molecules of water from these compounds separating black carbon as residue.

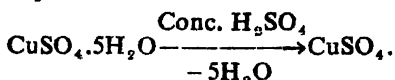


Oxalic acid

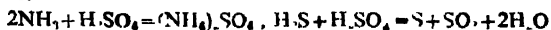


Cane sugar

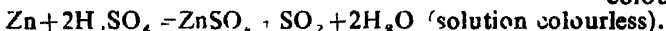
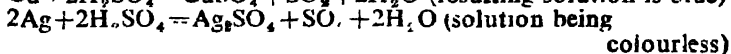
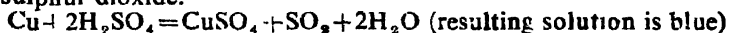
Concentrated sulphuric acid removes the water of crystallisation of the crystalline copper sulphate (blue) and turns it into anhydrous white powder.



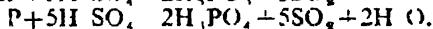
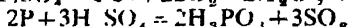
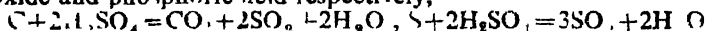
It is to be remembered that concentrated sulphuric acid can be used for drying gases like oxygen, sulphur dioxide, chlorine etc. which do not react with the acid. The acid can never be used for drying ammonia. Ammonia, being a basic substance, reacts with sulphuric acid forming the salt ammonium sulphate. H_2S , HBr , HI are oxidised by the concentrated acid to produce sulphur, bromine and iodine respectively while sulphuric acid is itself reduced to sulphur dioxide.



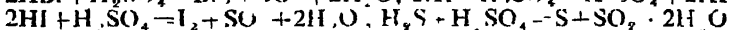
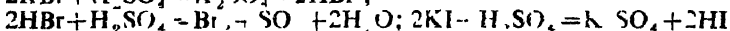
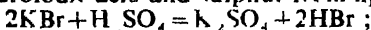
(4) Concentrated sulphuric acid possesses powerful oxidising properties. Hot and concentrated sulphuric acid oxidises metallic copper, silver, zinc etc. into their sulphates, it itself being reduced to sulphur dioxide.



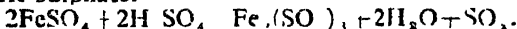
Carbon, sulphur, phosphorus on being treated with hot concentrated sulphuric acid are oxidised to carbon dioxide, sulphur dioxide and phosphoric acid respectively,



The concentrated acid liberates bromine from potassium bromide or hydrobromic acid, iodine from potassium iodide or hydroiodic acid and sulphur from hydrogen sulphide.

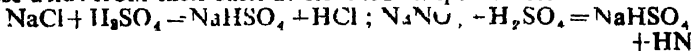


Hot, concentrated sulphuric acid oxidises ferrous sulphate into ferric sulphate.



While oxidising, sulphuric acid is itself reduced to sulphur dioxide.

(5) It is less volatile than hydrochloric or nitric acid and displaces these acids from their salts at elevated temperatures.



Experiments illustrating the important properties of sulphuric acid :

(1) Sulphuric acid decomposes at high temperature giving sulphur dioxide, oxygen and steam.



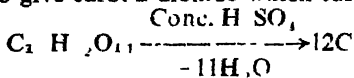
Concentrated sulphuric acid is dropped on strongly heated pumice stone taken in a round bottomed distilling flask. The resulting colourless, gaseous products evolving through the side tube are passed in succession through two U-tubes, the first one being kept immersed in water at ordinary temperature and the second in an ice-salt bath. The second U-tube is connected with a delivery tube. Two different liquids are found to collect in the two U-tubes and a colourless gas which comes out of the delivery tube is collected over water. The gas is proved to be oxygen by its power of rekindling a glowing chip of wood, forming brown fumes with nitric oxide and its absorption in alkaline pyrogallate solution. This proves conclusively that sulphuric acid contains oxygen. The colourless liquid collected in the first U-tube is shown to be water as it turns anhydrous copper sulphate (white) blue.

The colourless liquid in the second U-tube is condensed sulphur dioxide which can be detected by its characteristic suffocating odour of burning sulphur and its power of changing acidified orange yellow potassium dichromate solution green.

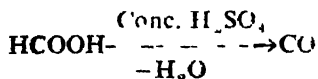
(2) *Sulphuric acid is an acid.* In a test tube, a dilute solution of sulphuric acid is prepared by adding a few drops of the acid to water. This aqueous solution turns blue litmus red. To a portion of the solution, zinc, magnesium or iron is added when a colourless gas is evolved. The evolved gas is hydrogen as it burns in the air with a blue flame.

The aqueous solution of the acid on being added to sodium carbonate or any other carbonate liberates carbon dioxide which can easily be detected by its ability to change clear lime water milky.

(3) *It is a strong dehydrating agent.* When concentrated sulphuric acid is added to a small amount of white, crystalline sugar in a test tube, the latter immediately turns black due to the separation of carbon. In this case, the elements of water of sugar are extracted by the concentrated acid leaving free carbon particles. The residue in the test tube is allowed to settle and poured into water slowly. The black mass is separated by filtration and burnt in air to give carbon dioxide which turns lime water milky.

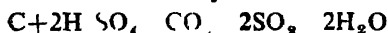


A mixture of formic acid and concentrated sulphuric acid on being heated in a test tube liberates carbon monoxide. When a lighted taper is held in the gas, the latter is found to burn with a blue flame at the mouth of the tube.



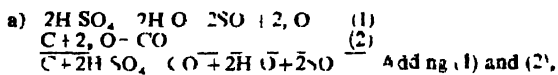
(4) *Sulphuric acid is an oxidising agent.* A mixture of concentrated sulphuric acid and powdered carbon is heated in a

round bottomed distilling flask. The resulting gaseous products coming out through the side tube are passed in succession through two U-tubes containing acidified yellow potassium dichromate solution and lime water respectively. It is found that the dichromate solution is turned green and the clear lime water milky. Inference can be drawn from these observations that sulphuric acid oxidises carbon into carbon dioxide while the acid itself is reduced to sulphur dioxide. Sulphur dioxide is absorbed in acidified dichromate solution and the unreacted carbon dioxide turns lime water milky

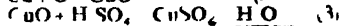


The oxidation reactions of sulphuric acid can be expressed by the following partial equations.

With carbon



With Cu $H_2SO_4 \rightarrow SO_2 + H_2O + O \quad (1)$



Adding (1), (2) and (3) we get $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

To prove that sulphuric acid contains hydrogen, sulphur and oxygen

Oxygen The decomposition of sulphuric acid to produce oxygen has been described (1st experiment) under the heading "experiment illustrating the important properties of sulphuric acid". This experiment proves conclusively that sulphuric acid contains oxygen.

Hydrogen A few pieces of granulated zinc are added to distilled water in a W. & A.'s bottle. No evolution of any gas takes place. On adding a little sulphuric acid to the content of the bottle, a colourless gas evolves. The gas is collected as usual by the displacement of water. The gas is identified to be hydrogen. When a lighted taper is introduced into the gas, the taper is extinguished but the gas burns with a blue flame.



Here, zinc displaces hydrogen from sulphuric acid.

Sulphur On heating concentrated sulphuric acid with copper turnings, sulphur dioxide gas is evolved. The gas dissolves in water giving sulphurous acid.



When sulphurous acid or the saturated aqueous solution of sulphur dioxide is heated in a sealed tube to 150°C, a light yellow solid separates. It is collected and dried. This solid substance can conclusively be proved to be sulphur. It dissolves in carbon disulphide and burns in the air yielding sulphur dioxide which is recognised by its smell of burning sulphur and its property of

turning orange yellow solution of acidified potassium dichromate green.

Thus, the experiment confirms the presence of sulphur in sulphuric acid.

Uses : Sulphuric acid is one of the most important chemicals used in industries as well as in laboratories.

(1) Sulphuric acid is used in the manufacture of hydrochloric acid, nitric acid; in the production of artificial manures like super phosphate of lime, ammonium sulphate and explosives like nitro glycerine, T.N.T., gun-cotton etc. (2) It is employed in the preparation of alums, useful metallic sulphates, various dyes and glucose from starch. (3) It is used in refining petroleum, in filling storage cells or accumulators and in washing iron before it is galvanized.

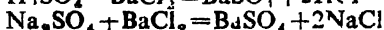
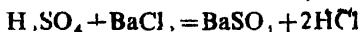
(4) Sulphuric acid is used in the laboratory for drying gases, for nitration of organic compounds and for the preparation of carbon monoxide, ethylene, ether etc.

(5) Fuming sulphuric acid is used as an oxidising and sulphonating agent of organic compounds.

Tests for sulphuric acid and sulphates

(i) Concentrated sulphuric acid on being heated with copper liberates sulphur dioxide which is detected by its characteristic suffocating smell of burning sulphur and ability to change the orange yellow solution of acidified potassium dichromate green.

(2) When barium chloride solution is added to dilute sulphuric acid or a sulphate solution, a white precipitate of barium sulphate insoluble in dil. or conc. HCl or HNO₃ is obtained.

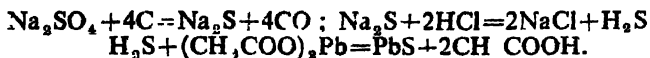


In the case of a water-insoluble sulphate, it is first fused with excess of sodium carbonate and the resulting mass is extracted with water. The filtrate after acidifying with dilute HCl is treated with barium chloride solution when a precipitate of barium sulphate is formed.



In fact, there is no reliable dry test for detection of the sulphate radical. The following dry test is sometimes performed for this purpose.

A small quantity of a sulphate is heated in a small cavity of a piece of charcoal by the reducing flame. The resulting mass when treated with dilute hydrochloric acid liberates hydrogen sulphide which is easily recognised by its smell of rotten egg. The gas also turns lead acetate solution black.



Black

CHAPTER 6

HYDRIDES OF NON-METALS

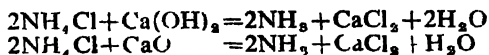
In this chapter, the chief hydrides of nitrogen, phosphorus, sulphur, chlorine, bromine and iodine have been discussed.

AMMONIA

Mol. formula NH_3 ,	Mol. wt. 17	Vapour density 8.5
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Priestly in 1774 prepared gaseous ammonia by heating lime with ammonium chloride which was known as 'Sal ammoniac' at that time. Priestly called it 'alkaline air'. In 1775 Berthelot analysed the gas and proved it to be a compound of nitrogen and hydrogen.

Preparation : (A) Laboratory method : In the laboratory, ammonia is usually prepared by heating a mixture of ammonium chloride and dry slaked lime or powdered quick lime.



An intimate mixture of 1 part by weight of ammonium chloride and 3 parts by weight of dry slaked lime is taken in a large hard glass test tube fitted with a delivery tube. About half of the tube is kept empty for the passage of the gas. The tube is then clamped

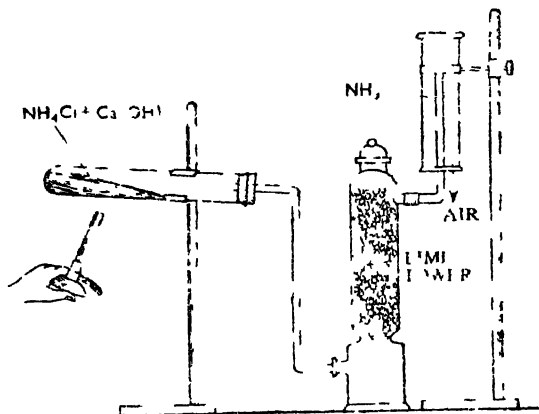


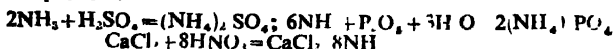
Fig. 2(64) Preparation of ammonia in the laboratory

to a stand in a slightly inclined position. The end of the delivery tube is attached to a glass tower [Fig. 2(64)] packed with quick lime. The mixture in the tube is carefully heated. The ammonia evolved is dried by passing it through the lime-tower and collected by the downward displacement of air in dry gas jars.

N.B. (1) Due to its high solubility in cold water, ammonia cannot be collected over water. The gas may be collected over mercury.

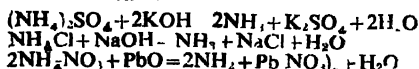
(2) Ammonia cannot be dried by concentrated sulphuric acid, phosphorus pentoxide or anhydrous calcium chloride, the common reagents used for drying gases.

Ammonia is a basic substance which reacts with sulphuric acid and phosphorus pentoxide (acidic oxide) producing ammonium sulphate and ammonium phosphate respectively. Again, anhydrous calcium chloride absorbs ammonia giving rise to an additive product.



So, the gas is conveniently dried by the basic drying agent quick lime.

(3) In fact, ammonia may be obtained by heating any ammonium salt with a strong alkali or a basic oxide.



(B) Preparation of ammonia in the laboratory at the ordinary

temperature : When strong aqueous solution of ammonia or liquor ammonia is added dropwise from a dropping funnel to solid caustic soda or caustic potash taken in a conical flask, ammonia gas comes out through the delivery tube.

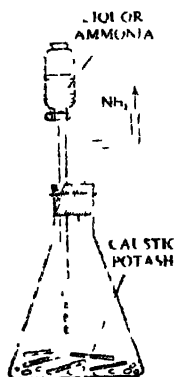
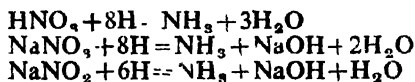


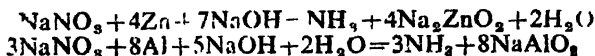
Fig. 2(65) Preparation of ammonia at ordinary temperature.

Other methods of preparation of ammonia :

(C) Ammonia can be obtained by reducing nitric acid, nitrates or nitrites by nascent hydrogen.



A nitrate (or a nitrite) can be quantitatively converted into ammonia by heating with zinc dust or aluminium and concentrated caustic soda solution.

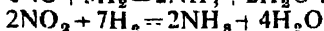
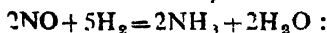


(D) Some ammonium salts decompose at high temperatures to give ammonia.

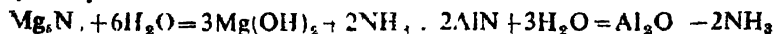


(E) Ammonia may also be obtained by passing a mixture of

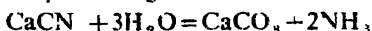
hydrogen and vapours of nitric acid of oxides or nitrogen except nitrous oxide over heated platinum catalyst.



(F) Ammonia is formed when some metallic nitrides are hydrolysed by hot water.



Super heated steam under pressure reacts with calcium cyanamide producing ammonia.



This method is regarded as a commercial method of preparation of ammonia.

Properties : Physical—(1) Ammonia is a colourless gas with a strong pungent smell. It can be easily liquefied by cooling on compression. At 10°C and under a pressure of 6 atmospheres, the gaseous ammonia is converted into a colourless liquid. Liquid ammonia has remarkable solvent properties and can be converted into an ice-like solid at -77.7°C . (2) It is lighter than air. (3) Ammonia is highly soluble in water. 1 volume of water at ordinary temperature and pressure dissolves 1300 volumes of the gas. The concentrated aqueous solution of ammonia is called liquor ammonia. It is very much harmful to eyes. So a bottle of liquor ammonia should always be cooled before opening the stopper. In a bottle of liquor ammonia, ammonia remains under high pressure. If the bottle is opened without cooling, some ammonia may spurt out due to release of pressure and fall into the eyes which may cause permanent blindness.

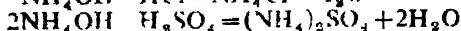
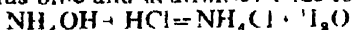
Chemical : (1) Ammonia is a stable compound but on prolonged heating at a very high temperature or sparking, the gas decomposes into its elements— nitrogen and hydrogen.



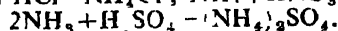
(2) Ammonia is a base. It dissolves in water forming an alkaline solution due to the formation of a weak alkali ammonium hydroxide. The compound dissociates in aqueous solution giving NH_4^+ and OH^- ions.



Aqueous solution of ammonia or ammonium hydroxide turns red litmus blue and neutralises acids to produce salts and water.

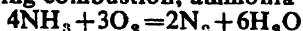


Ammonia gas also reacts with acids forming salts.

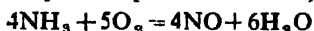


Ammonia in contact with hydrogen chloride gives dense white fumes of solid ammonium chloride. This reaction is an example of the formation of a solid product by the interaction of two gases.

(3) (a) Ammonia is not combustible in air and does not support combustion. But it burns in oxygen with a yellowish flame. During combustion, ammonia is oxidised to nitrogen.

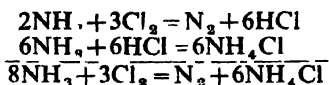


✓ (b) Ammonia is oxidised to nitric oxide when a mixture of ammonia and air or oxygen is quickly passed over heated platinum gauze catalyst (tempr. 500 – 700 C).

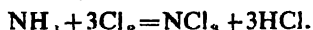


Nowadays, this reaction is utilised in the large scale production of nitric acid.

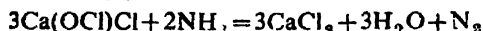
✓ (c) With chlorine, ammonia forms different products under different conditions. Chlorine reacting with excess of ammonia oxidises it to nitrogen. Chlorine is simultaneously reduced to hydrochloric acid. The acid formed reacts further with ammonia giving rise to ammonium chloride.



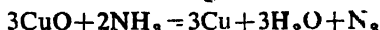
With excess of chlorine, ammonia forms nitrogen trichloride a highly explosive oily yellow liquid.



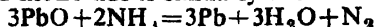
Bleaching powder oxidises ammonia to nitrogen.



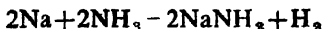
(4) Ordinarily, ammonia does not possess reducing properties. But it acts as a mild reducing agent at elevated temperature. When ammonia is passed over strongly heated black cupric oxide, the latter is reduced to metallic copper. Ammonia, on the other hand, is oxidised to nitrogen.



Lead monoxide is similarly reduced to metallic lead.



(5) Many metals at red heat react with ammonia. When dry ammonia is passed over heated sodium (about 400 C), one hydrogen atom of ammonia is replaced by sodium giving rise to sodamide. Hydrogen is evolved at the same time.



Sodamide is a wax-like solid which is decomposed by water producing ammonia and sodium hydroxide.



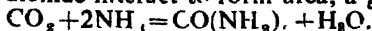
✓ Heated potassium reacts similarly with ammonia giving potashamid and hydrogen.

Magnesium on being heated in dry ammonia gives magnesium nitride (white solid) and hydrogen. $3\text{Mg} + 2\text{NH}_3 = \text{Mg}_3\text{N}_2 + 3\text{H}_2$. Calcium, however, forms calcium hydride and nitrogen.

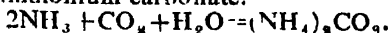
(6) Anhydrous calcium chloride, zinc chloride etc. absorb ammonia yielding addition-products such as $\text{CaCl}_2 \cdot 8\text{NH}_3$, $\text{ZnCl}_2 \cdot 8\text{NH}_3$.

(7) Ammonia reacts with carbon dioxide giving different products under different conditions.

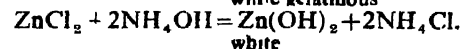
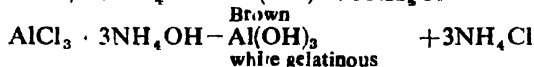
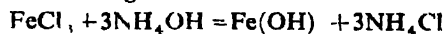
At 200 C and under 150 atm. pressure, gaseous ammonia and carbon dioxide interact to form urea, a good fertiliser.



Aqueous solution of ammonia reacts with carbon dioxide giving ammonium carbonate.

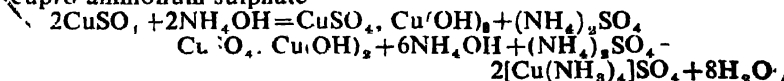


(8) Ammonium hydroxide or aqueous solution of ammonia precipitates the hydroxides of many metals when added to the solution of their salts. The colours of the hydroxides are sometimes helpful in detecting the metals.

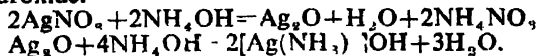


(9) In some cases, complex salts are formed when excess of ammonium hydroxide is added to the solution of some salts.

(a) When ammonium hydroxide is slowly added to copper sulphate solution, a pale blue precipitate of basic copper sulphate is first formed. On adding excess of ammonium hydroxide, the precipitate dissolves forming a deep blue solution of the complex cupro-ammonium sulphate



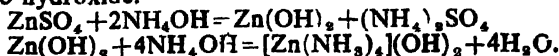
(b) Silver nitrate solution on being treated with ammonium hydroxide gives a white precipitate of silver hydroxide which quickly passes into the brown oxide, soluble in excess of ammonium hydroxide forming a clear solution of argento ammonium hydroxide.



(c) When ammonium hydroxide is added to silver chloride suspended in water, we get a clear solution of a soluble complex salt known as argento ammonium chloride.



(d) On adding ammonium hydroxide to zinc sulphate solution, we get a white precipitate of zinc hydroxide which dissolves in excess of ammonium hydroxide giving a clear solution of Zinc amino hydroxide.



Experiments to illustrate the important properties of ammonia :

(1) *Ammonia is exceedingly soluble in water and its aqueous solution reacts alkaline.*

Fountain experiment : A dry round-bottomed flask is filled with ammonia gas and closed with a rubber stopper through which passes a narrow long glass tube ending in a jet inside the flask. The flask is then clamped in an inverted position and the other end of the tube is dipped in water coloured with red litmus. Keeping the stop-cock open, the flask is cooled with ice-cold water when ammonia contracts creating a partial vacuum inside. As a result, the coloured water rises up and enters the flask in the form of a fountain and the colour of the liquid changes from red to blue. Thus, the solubility of ammonia in water and its alkaline character are proved simultaneously by this experiment.

(2) Ammonia (gas) forms solid ammonium chloride in contact with liquid or gaseous hydrochloric acid.

A piece of filter paper soaked in hydrochloric acid is plunged into a jar of ammonia when dense white fumes of ammonium chloride are formed inside the jar. $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$.

(3) *Ammonia is lighter than air.*

An empty jar (i.e. a jar containing air) is inverted over a gas jar full of ammonia and the cover plate is removed. Ammonia being lighter than air rises up and collects in the upper jar while the air travels in the lower jar. A piece of moist red litmus paper when introduced into the upper jar turns red. Moreover, dense white fumes of ammonium chloride are formed when a glass rod-moistened with concentrated hydrochloric acid is held in the gas.

(4) *Ammonia is neither a supporter of combustion nor combustible but it burns in oxygen.* If a lighted taper is introduced into a jar of ammonia, the taper is extinguished and the gas does not burn.

A wide glass tube is fitted at its bottom with a bored cork through which pass two glass tubes bent at right angles. One of the tubes is long and reaches the open end of the wide tube and the other is short and reaches just over the cork. Some cotton wool is loosely placed over the cork covering the inner end of the short tube. A stream of dry oxygen is then passed through the short tube so as to fill the wide tube with the gas. Dry ammonia is then passed through the long tube and is ignited, when ammonia continues to burn readily with a yellowish flame. [Fig. 2(67)]

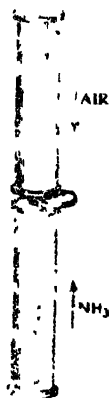
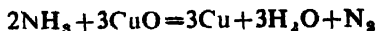


Fig.2(66) Ammonia is lighter than air

(5) *Ammonia acts as a reducing agent at high temperature.* Ammonia reduces heated cupric oxide to metallic copper and itself is oxidised to nitrogen



Ammonia is passed through an inlet tube attached to one end of a combustion tube containing red hot cupric oxide. The resulting gas coming out of the outlet tube attached to the other end is collected over water. When the reaction is complete, the tube is cooled to the room temperature. The red residue left in the tube is shown to be copper from its power of evolving brown fumes with nitric acid. The gas collected over water is found to be an inert one. When a lighted taper is introduced into the gas, the taper is extinguished. A piece of burning magnesium continues to burn in the gas producing a white powder (magnesium nitride) which on boiling with water gives off ammonia. Thus, it is proved that the gas is nitrogen. This experiment also conclusively proves that ammonia contains nitrogen.

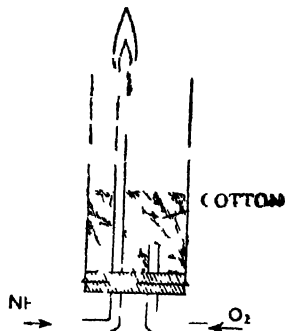


Fig. 2(67) Burning of ammonia

Uses: (1) In the laboratory, ammonia solution is used as an important reagent. (2) Liquid ammonia is used as a refrigerating agent especially in ice making. (3) Ammonia is largely employed for the manufacture of sodium carbonate by Solvay's process and nitric acid by Ostwald process. (4) Huge quantities of ammonia are required in the large scale production of fertilisers such as ammonium sulphate, ammonium phosphate, ammonium nitrate, urea etc. (5) Ammonia and ammonium salt are used in medicine and in the preparation of smelling salt $(\text{NH}_4)_2\text{CO}_3$ + a little lime water or any other alkali. (6) Ammonia is used as a cleansing agent for removing grease.

Principle underlying the use of ammonia in ice making Due to its easy volatility and high latent heat of vaporisation, liquid ammonia is widely used as a refrigerant in the manufacture of ice.

We know that anhydrous ammonia gas can be converted into liquid under high pressure and at the ordinary temperature. If the liquid is forced to pass through an expansion bulb and is allowed to expand suddenly, the evaporation of liquid ammonia is accompanied by the absorption of a large amount of heat from the surroundings. As a result, the surroundings get cooled. The use of ammonia in ice-making is based on this principle.

Anhydrous ammonia is first compressed under pressure by means of a compression pump and the compressed gas is passed through a spiral condenser cooled by a stream of cold water from outside to remove the heat generated due to compression. Ammonia condenses into a liquid which is allowed to pass through

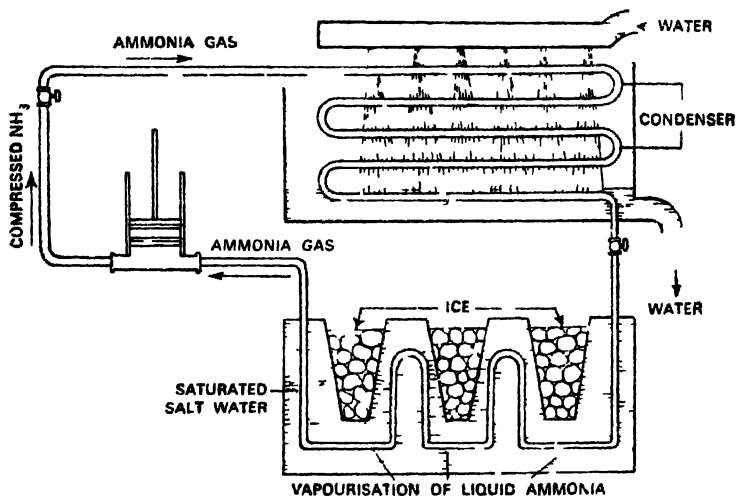


Fig. 2(67A) Manufacture of ice

an expansion valve into a long expansion coil kept immersed in brine in a large tank. Surrounding the expansion coil some tin cans containing clear water are placed. While passing through the large volume of the expansion coil, the pressure on the liquid ammonia is released and it vaporises rapidly. The heat absorbed during vaporisation lowers the temperature of brine below 0°C . As a result, the water in the tin cans is quickly cooled and freezes into ice. The ammonia gas from the expansion coils is again compressed and liquefied and the process is repeated.

Methyl chloride instead of ammonia may also be used as the refrigerant in ice-making.

Tests : (1) Ammonia can be detected by its basic character and strong pungent smell. It produces dense white fumes in contact with hydrogen chloride.

(2) A piece of paper soaked in mercuric chloride solution is blackened by ammonia.

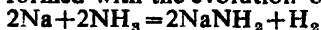
(3) It gives a brown solution or precipitate with Nessler's reagent. The presence of minute quantities of ammonia or ammonium salts can be detected by this reagent.

Nessler's reagent : On adding potassium iodide solution to mercuric chloride solution, a red precipitate of mercuric iodide is formed. The precipitate dissolves in excess of potassium iodide solution forming a soluble complex known as potassium mercuric iodide $[K_2HgI_4]$. Nessler's reagent is prepared by adding excess of potassium hydroxide to the solution of the complex salt.

Experiments to show that ammonia is a compound of nitrogen and hydrogen :

Nitrogen : The presence of nitrogen in ammonia has been shown under the experiment (No. 5) illustrating the reducing property of ammonia at high temperature.

Hydrogen : On passing dry ammonia gas over red hot sodium, sodamide is formed with the evolution of hydrogen.



Metallic sodium is kept in a hard glass long tube, one end of which is provided with a small inlet tube for passing ammonia and the other end with a delivery tube. Sodium in the tube is strongly heated and dry ammonia is passed over the molten sodium. The resulting gas issuing out of the delivery tube is collected over water. This gas is shown to be hydrogen by its inflammability in air with a blue flame. Thus, the presence of hydrogen in ammonia is conclusively proved.

PHOSPHINE OR PHOSPHORATED HYDROGEN

Mol. form. PH_3	Mol. wt. 34	Vap density 17
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Preparation : (A) Laboratory method : In the laboratory, phosphine is prepared by heating white phosphorus with a strong aqueous solution of caustic soda (or caustic potash). Phosphine is evolved as a gas and sodium hypophosphite formed remains in solution. $4P + 3NaOH + 3H_2O = PH_3 + 3NaH_2PO_2$.

Small pieces of white phosphorus and fairly strong solution of sodium hydroxide (30–40%) are taken in a flask fitted with a delivery tube and an inlet tube the end of which dips in the alkali solution. A current of coal gas or hydrogen or carbon dioxide is passed through the inlet tube to displace air completely from the flask. Now the flask is heated gently when phosphine containing traces of P_2H_4 is evolved and comes out of the delivery tube, the free end of which is kept under water. Each bubble of impure phosphine issuing from the delivery tube under water bursts into flame as soon as it comes in contact with air forming a vortex ring of white smoke of phosphorus pentoxide.

In fact, pure phosphine does

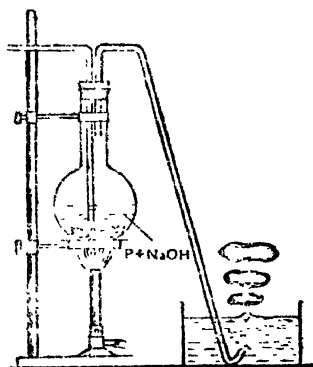
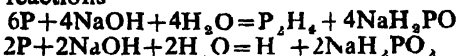


Fig. 2.66) Preparation of phosphine in the laboratory

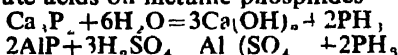
not ignite spontaneously in air. The spontaneous inflammability of phosphine prepared by the method just described is due to the presence of traces of highly inflammable P_2H_4 (phosphorus dihydride) in it. Sometimes, traces of hydrogen are also formed by side-reactions



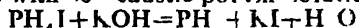
Phosphine is freed from P_2H_4 by passing the impure gas through a U-tube cooled in a freezing mixture when P_2H_4 condenses as a liquid. Phosphine passing over is collected over water.

N.B. (a) To avoid the ignition of impure phosphine in oxygen of the air the air inside the flask (in which the gas is prepared in the laboratory) is replaced by coal gas, H_2 or CO . When an alcoholic solution of caustic potash is used instead of the aqueous solution, P_2H_4 formed remains dissolved in alcohol. Thus non-spontaneously inflammable phosphine may be prepared,

(b) Impure phosphine can also be obtained by the action of water or dilute acids on metallic phosphides



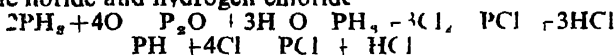
(c) Pure phosphine may be prepared by warming phosphonium iodide with 30% caustic potash solution



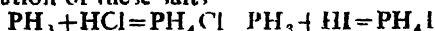
If phosphine (containing P_2H_4 and H_2) prepared in the laboratory is passed into a jar containing hydrogen iodide, solid phosphonium iodide is formed. Other hydrides and hydrogen may be easily removed as the gases and phosphine may be obtained in the pure state by treating the solid with caustic soda or caustic potash solution. The gas can be dried by solid caustic potash or phosphorus pentoxide and collected over mercury.

Properties Physical—(1) Phosphine is a colourless, poisonous gas with an unpleasant smell of rotten fish. (2) It is heavier than air and is sparingly soluble in water.

Chemical (1) Pure phosphine is not spontaneously inflammable in air. When heated to $150^\circ C$ it burns in air or oxygen with a mild explosion producing phosphine pentoxide and water. It ignites spontaneously in chlorine, yielding phosphorus trichloride, pentachloride and hydrogen chloride.



(2) Phosphine is a weakly basic compound. It is unable to change the colour of the litmus but forms phosphonium salts with halogen hydrides. The basic character of this compound is shown by the formation of these salts.

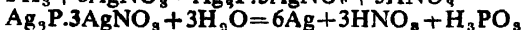
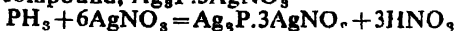


(3) When heated (at about $440^\circ C$), it decomposes into hydrogen and red phosphorus. $2PH_3 \rightarrow 2P + 3H_2$.

(4) *Phosphine is a strong reducing agent.* It precipitates the metals or the metallic phosphides when passed through the solution of copper, mercury and silver salts. It reduces copper sulphate to black copper phosphide in acidic solution.



When passed into silver nitrate solution, phosphine forms a black precipitate of metallic silver with the intermediate formation of a yellow compound, $\text{Ag}_3\text{P} \cdot 3\text{AgNO}_3$.



(5) Phosphine forms additive compounds such as AlCl_3 , PH_3 , CuCl , PH_3 with the chlorides of aluminium and copper.

Tests (1) It can be detected by its offensive smell of rotten fish. (2) The gas on being passed through a silver nitrate solution or acidified copper sulphate solution gives a black precipitate.

Comparison between ammonia and phosphine

Ammonia (NH_3)	Phosphine (PH_3)
(1) Colourless gaseous hydride with a characteristic pungent smell. Not poisonous.	(1) Colourless gaseous hydride with a distinctive odour of rotten fish. It is poisonous.
(2) Lighter than air.	(2) Heavier than air.
(3) Highly soluble in water forming the weak alkali ammonium hydroxide. The aqueous solution turns red litmus blue.	(3) Sparingly soluble in water. Fairly basic having no action on litmus.
(4) Basic in character, reacts with L_2 acids and oxyacids producing ammonium salts. $\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$ $2\text{NH}_3 + \text{H}_2\text{SO}_4 = (\text{NH}_4)_2\text{SO}_4$	(4) Feebly basic, reacts with halogen acids giving phosphonium salts. $\text{PH}_3 + \text{HCl} = \text{PH}_4\text{Cl}$ $\text{PH}_3 + \text{HI} = \text{PH}_4\text{I}$
(5) Ammonia is obtained by heating ammonium salts with strong alkalis [NaOH , KOH , Ca(OH)] etc.]	(5) Phosphine is obtained by warming phosphonium salts with caustic soda or caustic potash.
(6) Under the action of electric sparks, it decomposes into its elements hydrogen and nitrogen $2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$	(6) Decomposes into hydrogen and red phosphorus when subjected to the action of electric sparks $2\text{PH}_3 = 2\text{P} + 3\text{H}_2$
(7) Not inflammable and non-supporter of combustion but burns in excess of oxygen with a yellow flame $4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$	(7) Does not support combustion. Pure phosphine does not burn spontaneously but impure gas is spontaneously inflammable in the air. At 150°C , it burns in air or oxygen. $2\text{PH}_3 + 4\text{O}_2 = \text{P}_2\text{O}_5 + 3\text{H}_2\text{O}$
(8) Possesses reducing properties at elevated temperatures.	(8) Possesses strong reducing properties.
(9) Reacts with excess of chlorine giving nitrogen trichloride and hydrogen chloride. When NH_3 is in excess, nitrogen and NH_4Cl are formed.	(9) Spontaneously burns in chlorine yielding phosphorus tri- and penta chlorides.
(10) Precipitates some metals as hydroxides from the solution of their salts. Sometimes, soluble complex salts are formed.	(10) Precipitates the metals or the metallic phosphides when passed through solutions of copper, mercury, silver salts.

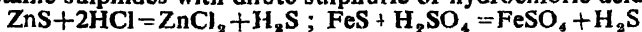
HYDROGEN SULPHIDE

(Sulphuretted hydrogen or Hydrosulphuric acid)

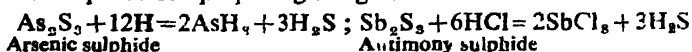
Mol. formula H_2S	Mol. wt. 34	Vap. density 17
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It is the most important gaseous hydride of sulphur. It occurs in volcanic gases and in certain spring waters. It is formed during the putrefaction of organic matter containing sulphur. The atmosphere contains traces of the gas.

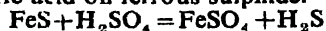
Preparation : (A) By the action of acids on the metallic sulphides : Generally, hydrogen sulphide is prepared by treating metallic sulphides with dilute sulphuric or hydrochloric acid.



In certain cases, nascent hydrogen generated by the action of acid on metals ($Zn + H_2SO_4$) or hot concentrated hydrochloric acid is required for preparing the gas.



Laboratory method : In the laboratory, hydrogen sulphide is most conveniently prepared by the action of cold, dilute sulphuric or hydrochloric acid on ferrous sulphide.



Some pieces of ferrous sulphide are taken in a two-necked Woulfe's bottle fitted with gas-tight corks. Through one of them

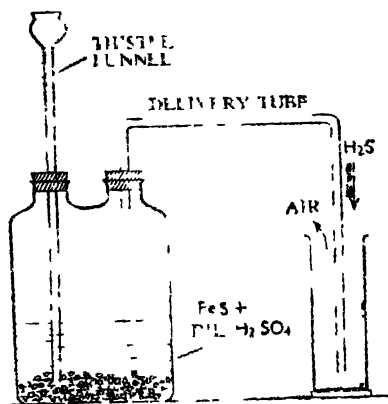


Fig. 2(69) Preparation of hydrogen sulphide in the laboratory

out through the delivery tube. As the gas is heavier than air, it is collected in gas-jars by upward displacement of air. It may also be collected over hot water.

Purification : The gas thus prepared is not pure. It always contains free hydrogen produced by the action of acid on iron invariably present in ferrous sulphide. Besides this, the gas

passes a thistle funnel reaching almost to the bottom of the bottle and through the other a bent delivery tube is introduced. Water is added down the thistle funnel so that the end of the funnel and ferrous sulphide dip under the liquid. The lower end of the delivery tube is kept well above the surface of water. Now, dilute hydrochloric or sulphuric acid is poured down the funnel and the bottle shaken slowly. The reaction starts as soon as ferrous sulphide comes in contact with the acid. Hydrogen sulphide evolves and begins to come

contains acid and water vapours. The gas is purified by passing in succession through

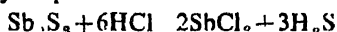
(a) a saturated solution of sodium hydrogen sulphide—to remove the acid vapours.



(b) a U-tube containing phosphorus pentoxide to absorb moisture.

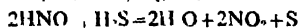
The dry gas is then cooled with solid carbon dioxide, when hydrogen sulphide liquefies and uncondensed hydrogen is removed by means of a pump. The liquid on slight warming is converted into the gaseous form and is collected.

Preparation of pure hydrogen sulphide : Pure hydrogen sulphide is obtained by the action of hot concentrated hydrochloric acid on antimony sulphide.

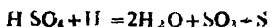


Antimony sulphide is taken in a round-bottomed flask fitted with a thistle funnel and a delivery tube. Concentrated hydrochloric acid is poured down the funnel so that the end of it remains under the surface of the liquid. On heating the flask, hydrogen sulphide comes out through the delivery tube. It is washed with water and dried by phosphorus pentoxide.

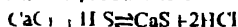
N. B. (1) Nitric acid cannot be used in the preparation of the gas from metallic sulphides, for the gas generated is oxidised into sulphur by nitric acid.



(2) Concentrated sulphuric acid is not used for drying the gas as the acid slowly oxidises it to sulphur. Concentrated acid is reduced to sulphur dioxide at the same time.



Fused calcium chloride is also not suitable for drying hydrogen sulphide as both of them react to produce calcium sulphide and hydrochloric acid.



It is best dried by alumina (Al_2O_3) or phosphorus pentoxide.

(3) The gas is not collected over mercury as it attacks the metal. However, dry and pure hydrogen sulphide does not react with mercury.

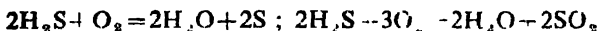
Preparation of hydrogen sulphide in the Kipp's apparatus : For obtaining an intermittent supply, the gas is prepared in a Kipp's apparatus. The description and working principle of the apparatus have been given in connection with the preparation of hydrogen. Small lumps of ferrous sulphide are taken in the central globe and dilute sulphuric acid is poured down the funnel attached to the upper globe.

The liquid left in the lower half-globe of the Kipp's apparatus or in the Woulfe's bottle used in the laboratory method is an impure solution of ferrous sulphate. The solution on evaporation gives the crystals of ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) which may be regarded as a by-product in the preparation of hydrogen sulphide.

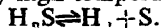
(B) **Synthetic method** : Pure hydrogen sulphide may be prepared by passing a mixture of hydrogen and sulphur vapour over finely divided nickel catalyst heated to 450 C or overheated pumice stone at 600 C. $H_2 + S \rightleftharpoons H_2S$

Properties : Physical - (1) Hydrogen sulphide is a colourless gas with a very unpleasant suffocating odour similar to that of a rotten egg. It is highly poisonous. (2) It is heavier than air. (3) The gas is moderately soluble in cold water imparting its own smell to the solution but it is not soluble in hot water. (4) It may be readily condensed to a colourless liquid by subjecting the gas to strong cooling or pressure.

Chemical. (1) *Hydrogen sulphide is a non supporter of combustion but burns in air or oxygen with a blue flame.* Combustion of hydrogen sulphide in a limited supply of oxygen gives sulphur and steam whereas if the gas is burnt in plentiful supply of air, sulphur dioxide and steam are obtained.

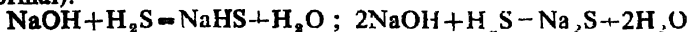


(2) *The gas decomposes into its elements hydrogen and sulphur at a very high temperature or when sparked.*

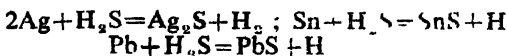


(3) In aqueous solution, hydrogen sulphide behaves as a weak, dibasic acid and turns blue litmus slightly red. The solution is a better conductor of electricity than water showing that ionisation takes place. $H_2S \rightleftharpoons H^+ + HS^- \rightleftharpoons 2H^+ + S^{2-}$

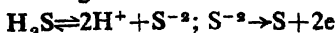
It reacts with bases or alkalis to form salts. With alkalis it forms two types of salts, hydrosulphides (acid salts) and sulphides (normal).



Certain metals displace its hydrogen forming the metallic sulphides.



(4) *Hydrogen sulphide acts as a good reducing agent.* Its reducing character is primarily due to the oxidation of S^{2-} ion into elementary sulphur. Like all reducing agents, it operates as a supplier of electrons. The usual product is a precipitate of sulphur arising from the changes.



It reduces chlorine, bromine or iodine suspended in water to the corresponding halogen hydrides, it itself being oxidised to sulphur.

$$Cl_2 + H_2S = 2HCl + S \downarrow ; I_2 + H_2S = 2HI + S \downarrow$$

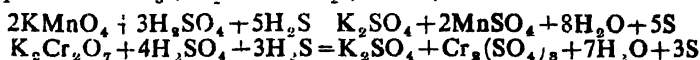
With excess of chlorine water, it is oxidised into sulphuric acid

$$H_2S + 4H_2O + 4Cl_2 = H_2SO_4 + 8HCl$$

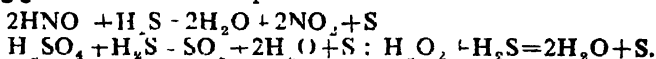
Yellow solution of ferric chloride is reduced by hydrogen sulphide to a colourless solution of ferrous chloride. Trivalent iron is converted into bivalent iron during the reduction. Hydrogen

sulphide reduces the pink solution of acidified potassium permanganate to a colourless solution of manganous salt. It also reduces a solution of potassium dichromate acidified with dilute sulphuric acid into a solution of chromic salt; the colour of the solution changes from orange yellow to green.

During the reduction processes, heptavalent manganese is converted into its bivalent state and hexavalent chromium into its trivalent state. In all these cases, hydrogen sulphide is oxidised to sulphur. $2\text{FeCl}_3 + \text{H}_2\text{S} = 2\text{FeCl}_2 + 2\text{HCl} + \text{S}$



Hydrogen sulphide also shows its reducing properties when allowed to act upon conc. nitric acid, conc. sulphuric acid and hydrogen peroxide. Concentrated nitric and sulphuric acids are reduced to nitrogen dioxide (brown gas) and sulphur dioxide respectively. Hydrogen peroxide is reduced to water while the remaining gas is oxidised to sulphur.

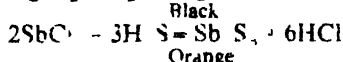
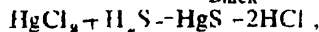
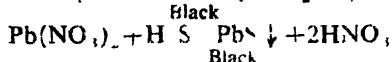
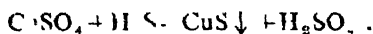


Moist sulphur dioxide and hydrogen sulphide react together producing sulphur. This is also a redox reaction.



N. B. Sulphur dioxide and hydrogen sulphide show similarities in their reducing properties. Acidified potassium permanganate and dichromate solutions are reduced by both the gases. The effect produced by H_2S differs from that produced by SO_2 because, while either gas decolourises the permanganate and turns the dichromate from orange yellow to green, hydrogen sulphide also leaves a precipitate of sulphur but sulphur dioxide does not. It is oxidised to sulphuric acid in these cases.

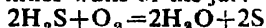
(5) Hydrogen sulphide precipitates the sulphides of many metals from the aqueous solution of their salts.



Experiments to illustrate some of the properties of hydrogen sulphide :

(1) *It is soluble in water and the aqueous solution reacts acidic.* A test tube filled with hydrogen sulphide is inverted over water when the water rises up the tube slowly. When a piece of blue litmus paper is introduced into the solution, the paper turns slightly red. This proves that the gas is soluble in water, giving an acidic solution.

(2) *Hydrogen sulphide is combustible but does not support combustion.* When a lighted taper is introduced into a jar of hydrogen sulphide, the taper is at once extinguished but the gas burns at the mouth of the jar with a blue flame. Solid sulphur is deposited in the inner walls of the jar.



(3) *It is a strong reducing agent.* Ferric chloride solution, acidified potassium permanganate solution and potassium dichromate solution containing a little dilute sulphuric acid are taken separately in three test tubes and hydrogen sulphide is passed through each of the solutions. There is a notable change of colour in each case. The yellow ferric chloride solution is changed into a colourless solution. The pink colour of the permanganate solution disappears and the orange yellow solution of potassium dichromate turns green. Yellow sulphur is precipitated in the three tubes. (Explanation and equations of the reactions have been given in connection with the properties of hydrogen sulphide)

The use of hydrogen sulphide : Hydrogen sulphide is used as a very important reagent in qualitative analysis of inorganic salts. Sulphides of many metals are insoluble in water. So, when hydrogen sulphide is passed into the aqueous solution of salts of such metals, they are precipitated as their insoluble sulphides. Some of these sulphides often have characteristic colours. For instance,

Cupric sulphide (CuS)—Black

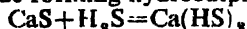
Mercuric sulphide (HgS) .. Cadmium sulphide (CdS) yellow

Lead sulphide (PbS)— .. Antimony sulphide (Sb_2S_3)—Orange

Arsenic sulphide (As_2S_3)—yellow ; Zinc sulphide (ZnS)—white.

The characteristic colours of the sulphides often help us in identifying the respective metals.

Some of the metallic sulphides such as CuS , PbS are insoluble in hydrochloric acid. Zinc sulphide, iron sulphide etc. are soluble in dil. HCl but insoluble in solution made alkaline with ammonium hydroxide containing NH_4Cl . Certain sulphides, such as Na_2S , K_2S , $(\text{NH}_4)_2\text{S}$ are soluble equally in water, dilute mineral acids and alkalis. Calcium and magnesium sulphides are sparingly soluble in water but dissolve in aqueous solution of hydrogen sulphide forming hydrosulphides.



For qualitative chemical analysis, the metallic sulphides have been divided into three classes :

(1) the sulphides which are insoluble in dilute hydrochloric acid and precipitated from solutions acidified with dilute HCl .

(2) the sulphides which are insoluble in ammoniacal solution and are precipitated from solutions made alkaline with ammonium hydroxide.

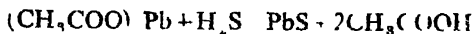
(3) the sulphides which are equally soluble in water, dilute acids, alkalis and are not precipitated from solutions.

Taking advantage of the different solubilities of the sulphides, the metals can be separated from a mixture of their salts. Let us analyse an aqueous solution containing copper sulphate, zinc sulphate and sodium sulphate. Hydrogen sulphide is passed into the solution rendered acidic by means of dilute hydrochloric acid when copper sulphide (black) is only precipitated. The precipitate is filtered off. The filtrate is boiled and is made alkaline by ammonium hydroxide. On passing hydrogen sulphide through this alkaline solution, we get the white precipitate of zinc sulphide. The resulting filtrate will contain the sodium salt only. Thus, hydrogen sulphide permits the separation of metals from solution of their salts.

When two or more sulphides have the same colour, they are identified with the help of various reagents. For instance, both copper sulphide and mercuric sulphide are black in colour. But copper sulphide is soluble in hot dilute nitric acid whereas mercuric sulphide remains unaffected in this acid.

In this connection, it must be remembered that the precipitation of sulphides of the metals by hydrogen sulphide depends on many factors such as nature and concentration of the acid, alkali etc. and on the concentration of H^+ and OH^- ions.

Tests. (1) Hydrogen sulphide is easily detected by its characteristic disagreeable smell of rotten eggs. (2) It rapidly blackens a piece of paper soaked in lead acetate solution due to the formation of lead sulphide.



(3) The gas produces a nice violet colour with alkaline sodium nitroprusside solution. (It is noted that hydrogen sulphide does not change the colour of sodium nitroprusside solution. It responds to this test only when it forms an alkaline sulphide with an alkali.) (4) A silver coin is stained black in contact with the gas due to the formation of a film of silver sulphide.

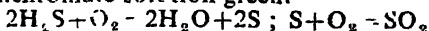
Tests for metallic sulphides: Dry Test. On adding dilute hydrochloric or sulphuric acid (cold and sometimes hot) to a metallic sulphide, hydrogen sulphide is evolved which is detected by its peculiar smell and by its action on lead acetate paper. In some cases, H_2S is liberated from the sulphides by the action of nascent hydrogen ($Zn + H_2SO_4$).

Wet test: The aqueous solution of a metallic sulphide on being made alkaline by sodium hydroxide solution is treated with a few drops of freshly prepared solution of sodium nitroprusside. A purple colouration is produced.

To prove that hydrogen sulphide contains sulphur and hydrogen:

Sulphur: A lighted taper is introduced into a jar of hydrogen sulphide when the taper is at once extinguished but the gas burns

at the mouth of the jar. A yellow solid is deposited in the inner walls of the jar. The yellow solid can conclusively be proved to be sulphur by its solubility in carbon disulphide. Further the solid burns in air producing sulphur dioxide (having a characteristic suffocating smell) which turns a piece of paper soaked in acidified potassium dichromate solution green.



Hydrogen : A few c.c. of hydrogen sulphide are collected over mercury in a thumb tube which is kept over the same metal in a trough. A piece of tin is introduced into the horizontal part of the tube. Now the tin is heated in the atmosphere of hydrogen sulphide when a solid product (stannous sulphide) is obtained. The remaining gas inside the tube can be shown to be hydrogen by the following test.

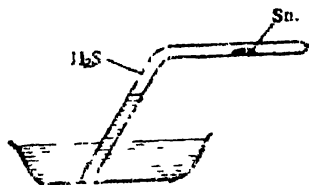


Fig. 2(70)

The gas burns in air with a blue flame and produces water which turns white anhydrous copper sulphate blue.

Thus, the above experiments illustrate that hydrogen sulphide contains sulphur and hydrogen.

HYDROGEN CHLORIDE, HCl

In 1772, Priestley first prepared the compound from the sea salt and termed it marine acid air (muriatic acid). Davy in 1810 established that it is a compound of hydrogen and chlorine and gave the name hydrogen chloride. The aqueous solution of it is acidic and is called hydrochloric acid.

Preparation : From metallic chlorides :

(A) **Laboratory method :** In the laboratory, hydrogen chloride is usually prepared by heating a mixture of common salt (sodium chloride) and concentrated sulphuric acid. The reaction takes place in two stages depending upon the temperature. At comparatively lower temperature (150° – 200°C), hydrogen chloride and sodium bisulphate are formed; the latter at much elevated temperature (above 500°C) reacts with sodium chloride giving sodium sulphate and more hydrogen chloride.

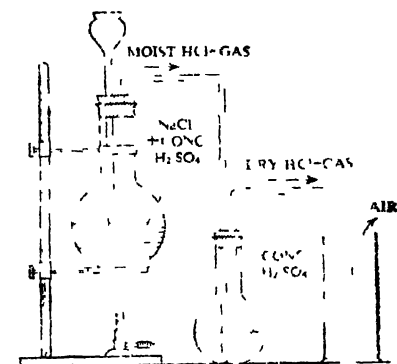
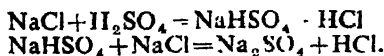
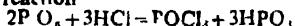


Fig. 2(71) Preparation of hydrogen chloride in the laboratory

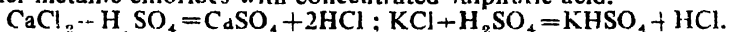
In the laboratory, the first stage of the reaction is only allowed to occur.

Sodium chloride is taken in a round-bottomed flask provided with a thistle funnel and a delivery tube, the outer end of which dips in concentrated sulphuric acid in a wash bottle. The wash bottle is fitted with another delivery tube, the free end of which is introduced almost to the bottom of a dry gas jar. Concentrated sulphuric acid is poured down the funnel so that the end of it dips under the surface of the liquid. The flask is then gently heated when hydrogen chloride evolves and passes out through the delivery tube. The issuing gas is freed from moisture while passing through the conc. sulphuric acid and is collected by upward displacement of air. The gas may also be collected over mercury.

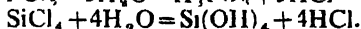
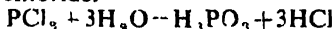
N.B. Hydrogen chloride cannot be dried by phosphorus pentoxide because of the following reaction



(B) Hydrogen chloride may also be obtained by heating other metallic chlorides with concentrated sulphuric acid.



Some non-metallic chlorides on being reacted with water give hydrogen chloride.



Preparation of aqueous solution : Hydrogen chloride is exceedingly soluble in water and its aqueous solution called hydrochloric acid is prepared by dissolving the gas carefully in water. Hydrogen chloride generated in the flask as in Fig. 2(71) is led through an empty flask and is allowed to dissolve in water through a funnel, the stem of which is connected with the end of the delivery tube. Care is taken to see that the mouth of the funnel just dips under the surface of water in the beaker. This arrangement is made to eliminate the possibility of antisuction. If the gas is directly led into water without passing through the empty flask, there may be a reduction of pressure inside the apparatus due to the great solubility of hydrogen chloride and water from the beaker may be sucked back into the reaction mixture in the flask causing explosion.

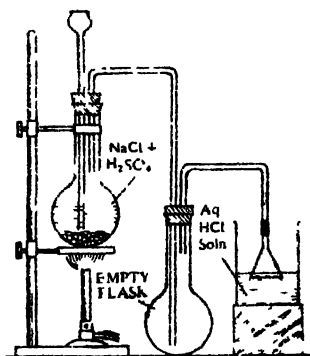


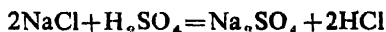
Fig. 2(72) Preparation of aqueous HCl

(C) **Synthetic method :** Hydrogen chloride may be synthesised by exposing a mixture of equal volumes of hydrogen and chlorine to direct sunlight or by heating the mixture. It may also be prepared by burning a jet of hydrogen in a jar of chlorine gas.

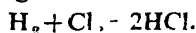


Manufacture of hydrochloric acid : Manufacture of this acid is not included in the syllabus. So only the outlines of the commercial processes are mentioned here.

(1) **Le Blanc process :** Hydrochloric acid was formerly manufactured by heating common salt with concentrated sulphuric acid at 600°C in a similar method as used in the laboratory preparation.



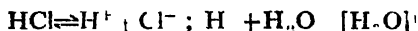
(2) **Synthetic method :** The manufacture of the acid by direct combination of chlorine and hydrogen obtained as by-products in the commercial production of caustic soda is nowadays much in use. A mixture of nearly equal volumes of hydrogen and chlorine is fed into a burner similar to oxy-hydrogen blow pipe placed in a combustion chamber made of silica bricks. The resulting hydrogen chloride is cooled and then dissolved in water.



Properties : Physical—(1) Hydrogen chloride is a colourless gas with a suffocating odour. It strongly fumes in moist air. (2) It is 1.3 times heavier than air. (3) It is extremely soluble in water. It is also soluble in organic liquids like alcohol, acetic acid etc. (4) Hydrogen chloride can be readily liquefied into a colourless liquid by application of pressure and cooling.

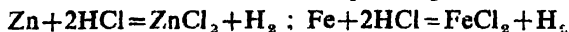
Chemical : (1) *Hydrogen chloride neither burns in air nor supports combustion.* However, burning sodium continues to burn in the gas with a bright yellow flame producing hydrogen and anhydrous sodium chloride. $2\text{Na} + 2\text{HCl} = 2\text{NaCl} + \text{H}_2$.

(2) *Its aqueous solution is strongly acidic and turns blue litmus red.* It is a monobasic acid. In dilute aqueous solution, it completely ionises into hydrogen and chloride ions and conducts electricity.



In fact, the ion responsible for acidity is not the simple H^+ ion but a hydrated form of it, the hydroxonium ion H_3O^+ . The salts of this acid are called the chlorides such as KCl , ZnCl_2 , AlCl_3 , etc. All metallic chlorides with the exception of PbCl_2 , AgCl and Hg_2Cl_2 are soluble in water.

Metals like zinc, magnesium, tin, iron etc. dissolve in hydrochloric acid at the ordinary temperature with the evolution of hydrogen and formation of the corresponding metallic chlorides.

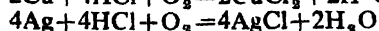
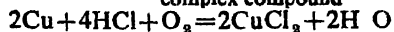


The metals which stand above hydrogen in the electrochemical series can only displace hydrogen from the dilute acid.

Generally, silver, mercury, gold are not attacked by hydrochloric acid. Copper and lead dissolve in hot and concentrated acid. In presence of air copper and silver react with the acid very slowly.

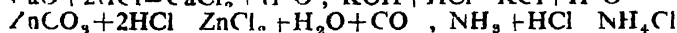


complex compound



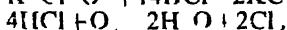
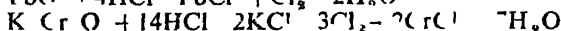
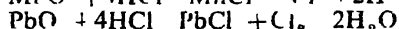
Gold or platinum does not react with the acid. Liquid hydrogen chloride does not conduct electricity and has no action upon litmus or metals in the absence of water. However, aluminium dissolves in the liquid.

Hydrochloric acid reacts with metallic oxides and hydroxides yielding salts and water. It liberates carbon dioxide from a carbonate and forms ammonium chloride with ammonia gas or ammonium hydroxide.

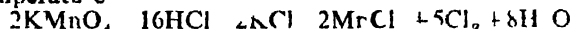


13. When a dilute solution of hydrochloric acid is distilled the water evaporates and the concentration of the solution increases. But concentrated hydrochloric acid on distillation gives off hydrogen chloride first and resulting solution becomes more diluted. Anhydrous (anhydrous) hydrochloric acid on distillation produces ultimately a solution of about 20% of HCl. We call this solution 'fuming hydrochloric acid' at a temperature of (110°C). The acid of this strength is a constant boiling mixture.

(3) Hydrochloric acid is readily oxidised into chlorine. It reacts like manganese dioxide, lead dioxide, potassium dichromate, convert hot concentrated acid into chlorine. Air or oxygen in presence of copper chloride catalyst oxidises the acid to form chlorine.

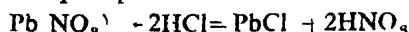


Potassium permanganate oxidises the acid at the ordinary temperature.

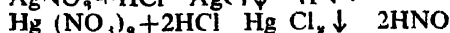


But hydrochloric acid is not oxidised by concentrated sulphuric acid.

(4) When hydrochloric acid or an aqueous solution of a metallic chloride is added to a solution of lead, silver or mercurous salt, a white precipitate of the chloride of the metal is obtained.



Lead chloride is soluble in boiling water.



5. A mixture of concentrated hydrochloric acid and concentrated nitric acid in the ratio of 3:1 by volume is called *aqua regia* which dissolves the noble metals like gold, platinum etc.

(5) Concentrated hydrochloric acid on electrolysis liberates hydrogen at the cathode and chlorine at the anode.

Experiments illustrating the important properties of hydrogen chloride :

(1) *Hydrogen chloride is neither combustible nor a supporter of combustion.* When a lighted taper is introduced into a jar of hydrogen chloride, the taper is extinguished and the gas does not burn.

(2) *It is highly soluble in water and the aqueous solution reacts acidic.* The solubility in water and acidity of the solution of hydrogen chloride can be proved by the fountain experiment. The experimental procedure has been described while illustrating the similar properties of sulphur dioxide. In this case, the flask is only filled with hydrogen chloride instead of sulphur dioxide.

(3) (a) It reacts with ammonia gas giving ammonium chloride. A glass rod moistened with concentrated ammonia solution or liquor ammonia is brought near a glass jar containing hydrogen chloride when dense white fumes of ammonium chloride is obtained. $\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$.

(b) A small amount of calcium carbonate taken in a test tube is treated with dilute hydrochloric acid when a colourless, odourless gas is evolved. That the gas is carbon dioxide is proved by the fact that it turns clear lime water milky. Thus, the experiment illustrates that hydrochloric acid liberates carbon dioxide from a carbonate.

(c) The metals such as zinc, magnesium etc. dissolves in dilute hydrochloric acid with the evolution of hydrogen. A little dilute hydrochloric acid is taken in a test tube and a piece of granulated zinc is added to it. The acid and the metal react immediately liberating a colourless, odourless gas. The gas is shown to be hydrogen by its inflammability with a blue flame.

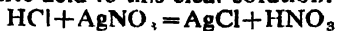
(4) *It is oxidised to chlorine by oxidising agents.*

Hydrogen chloride is passed through an inlet tube attached to one end of a combustion tube containing heated manganese dioxide. A greenish yellow gas is found to escape from the other end of the tube. The issuing gas is chlorine as it turns a piece of paper soaked in potassium iodide and starch solutions deep blue. Hydrogen chloride may also be converted into chlorine if crystals of potassium dichromate are used in the combustion tube in place of manganese dioxide.

Uses : Hydrochloric acid is widely used in the laboratories and industries. In respect of its industrial applications, it stands next to sulphuric acid. (1) It is employed in the manufacture of various useful metallic chlorides, chlorine and dyes. (2) Hydrochloric acid finds its application in medicine, in removing the oxide scale from iron sheets before galvanization, in the preparation of glucose from starch. (3) It is used in preparing aqua regia to dissolve gold and platinum.

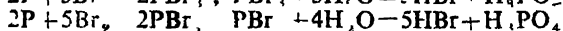
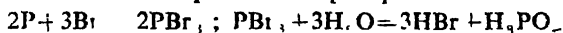
Test: (1) Hydrogen chloride forms dense white fumes of ammonium chloride in contact with ammonia. (2) Concentrated hydrochloric acid or any metallic chloride on being heated with manganese dioxide and concentrated sulphuric acid liberates greenish yellow chlorine gas which turns moist starch iodide paper blue.

(3) When silver nitrate solution is added to hydrochloric acid or an aqueous solution of a metallic chloride, a curdy white precipitate of silver chloride is formed. The precipitate is insoluble in nitric acid but dissolves in ammonium hydroxide forming a clear solution of a soluble complex salt. The precipitate reappears on adding nitric acid to this clear solution.



HYDROGEN BROMIDE, HBr

Preparation: (A) **Laboratory method**—In the laboratory, hydrogen bromide is prepared by the action of bromine on a mixture of red phosphorus and water. By the interaction of red phosphorus and bromine, phosphorus tribromide and pentabromide are first formed which then suffer hydrolysis evolving hydrogen bromide. Phosphorus and phosphoric acids are also formed.



A mixture of red phosphorus and water is taken in a round-bottomed flask fitted with a dropping funnel and a delivery tube. Bromine is added drop by drop from the dropping funnel into the mixture when reaction takes place vigorously evolving hydrogen bromide gas. The issuing gas is first led through a U-tube filled with glass beads covered with moist red phosphorus and then through a bulb containing anhydrous calcium chloride or CaBr_2 (the bulb has not been shown in the fig). Moist red phosphorus eliminates any bromine vapour that may escape from the flask and CaCl_2 absorbs the water vapour. The pure, dry hydrogen bromide is collected by the upward displacement of air. The gas may also be collected over mercury.

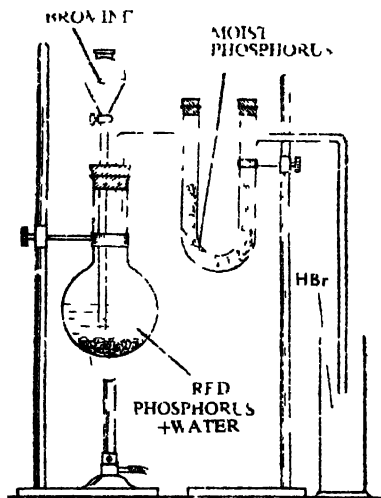
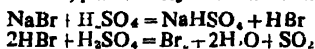
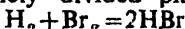


Fig. 2(73) Preparation of hydrogen bromide in the laboratory

N. B. Hydrogen bromide cannot be prepared by heating a bromide with concentrated sulphuric acid in a similar method as used in preparing hydrogen chloride. Hydrogen bromide liberated initially is oxidised by concentrated sulphuric acid into bromine, particularly when heated.



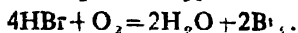
(B) **Synthetic method:** Hydrogen and bromine do not combine even in bright sunlight. But hydrogen bromide may be prepared synthetically by passing a mixture of hydrogen and bromine-vapour over finely divided platinum catalyst heated to 200°C .



Preparation of aqueous solution or hydrobromic acid: To get an aqueous solution of hydrogen bromide or hydrobromic acid, the end of the delivery tube of the Fig 2(73) is connected with the stem of a funnel, the mouth of which just touches the surface of water in a beaker. The issuing hydrogen bromide directly dissolves in water giving rise to its aqueous solution.

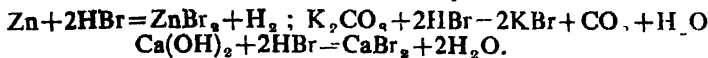
Properties : Physical—(1) Hydrogen bromide is a colourless gas with a strong irritating smell. It fumes in the moist air. (2) It is much heavier than air (density being almost three times than that of air).

Chemical : (1) Hydrogen bromide on being heated to 500°C decomposes into its elements. $2\text{HBr} \rightleftharpoons \text{H}_2 + \text{Br}_2$ (2) Its vapour is neither combustible nor a supporter of combustion. (3) It is exceedingly soluble in water giving a strongly acid solution but is less stable than hydrochloric acid. The solution is oxidised into bromine even by atmospheric oxygen in sunlight.

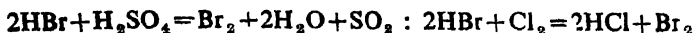


The salts of the acid are called bromides—such as potassium bromide (KBr), zinc bromide (ZnBr_2) etc. All bromides except AgBr , PbBr_2 and Hg_2Br_2 are soluble in water.

Hydrobromic acid is a monobasic acid which turns blue litmus red. Hydrobromic acid on being reacted with iron, zinc and some other metals gives off hydrogen. Potassium reacts vigorously with liberation of hydrogen. As an acid, it liberates carbon dioxide from carbonates or bicarbonates and neutralises bases to form salts and water. $2\text{K} + 2\text{HBr} = 2\text{KBr} + \text{H}_2$.



(4) It is readily oxidised into bromine by the oxidants like manganese dioxide, potassium permanganate, sulphuric acid, chlorine etc.



The above reactions indicate that sulphuric acid has oxidised hydrogen bromide into bromine whereas the acid itself has undergone reduction to produce sulphur dioxide. Similarly while oxidising, chlorine suffers reduction giving hydrochloric acid.

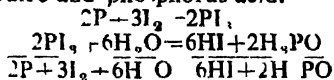
Tests for hydrobromic acid or metallic bromides : (1) Hydrobromic acid or any metallic bromide when heated with concentrated sulphuric acid gives off red vapours of bromine. Addition of manganese dioxide expedites the reaction. The vapours turn a piece of paper soaked in potassium iodide and starch solutions blue.

(2) When hydrobromic acid or a solution of any metallic bromide in presence of a little carbon disulphide or carbon tetrachloride is shaken with chlorine water, the layer of organic solvent turns reddish brown due to the liberation of bromine.

(3) When silver nitrate solution is added to hydrobromic acid or an aqueous solution of any metallic bromide, a pale yellow precipitate of silver bromide is obtained. The precipitate is insoluble in nitric acid but soluble in ammonium hydroxide with difficulty.

HYDROGEN IODIDE, HI

Preparation (A Laboratory method—In the laboratory, hydrogen iodide is usually prepared by the action of water on a mixture of requisite amounts of red phosphorus and iodine. By the interaction of red phosphorus and iodine phosphorus tri-iodide is first formed which then suffers hydrolysis with water producing hydrogen iodide and phosphorus acid.



A mixture of red phosphorus and iodine is taken in a round-bottomed flask fitted with a dropping funnel and a delivery tube. Water from the funnel is dropped cautiously into the mixture when hydrogen iodide is evolved and comes out through the delivery tube. The issuing gas is first passed through a U-tube containing glass beads coated with moist red phosphorus and then through a bulb containing phosphorus pentoxide. Red phosphorus and phosphorus pentoxide absorb iodine vapour and moisture respectively (CaI_2 may also be used in drying the gas). The dried, pure hydrogen iodide is collected by upward displacement of air.

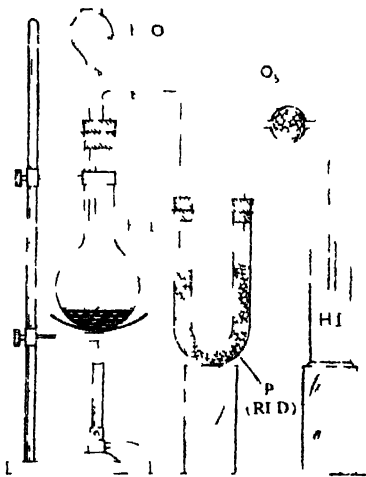
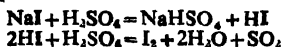


Fig 2(74) Preparation of hydrogen iodide in the laboratory

N.B. (1) Hydrogen iodide cannot be prepared by the action of hot concentrated sulphuric acid on an iodide in a similar method as used in the preparation

of hydrogen chloride. The reason is that the hydrogen iodide formed initially is oxidised to iodine by concentrated sulphuric acid. Sulphur dioxide is also formed as one of the products due to the reduction of sulphuric acid.



(2) On heating an iodide with phosphoric acid (H_3PO_4), hydrogen iodide may be obtained. Phosphoric acid is not an oxidising agent and there is no secondary reaction as in the case of conc. H_2SO_4 .



(3) Hydrogen iodide cannot be collected over mercury as the gas attacks the metal.

(B) **Synthetic method :** Hydrogen iodide may be synthesised by passing a mixture of hydrogen and iodine-vapour over heated platinum catalyst. This is a reversible reaction. As the hydrogen iodide is easily dissociated into its elements under the influence of heat, hydrogen and iodine may only combine partially to yield hydrogen iodide by this process. $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$.

Preparation of aqueous solution or hydroiodic acid :

(1) Hydrogen iodide prepared by the laboratory method is passed into water in a beaker through a funnel attached to the end of the delivery tube. Hydrogen iodide dissolves directly in water producing its aqueous solution.

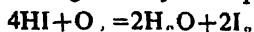
(2) The aqueous solution of the gas or hydroiodic acid may also be obtained by bubbling hydrogen sulphide into a suspension of iodine in water. $\text{H}_2\text{S} + \text{I}_2 \rightarrow 2\text{HI} + \text{S} \downarrow$

The solution is filtered from the precipitated sulphur.

Properties : Physical—(1) Hydrogen iodide is a colourless gas with a characteristic pungent smell. It fumes strongly in moist air.
(2) It is much heavier than air.

Chemical : (1) *It decomposes readily into its elements* on heating or when exposed to sunlight. Thus, violet vapours of iodine are seen when a heated glass rod is introduced in a gas-jar of hydrogen iodide. $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$

(2) It is extremely soluble in water and the aqueous solution reacts acidic. This colourless solution is known as hydroiodic acid. It is less stable than hydrochloric acid. Hydroiodic acid is decomposed and oxidised into iodine by oxygen of the air in sunlight. Thus, freshly prepared colourless solution of hydroiodic acid turns brown gradually on exposure to air.



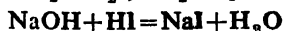
The salts of the acid are called iodides—such as sodium iodide (NaI), magnesium iodide (MgI_2) etc.

All metallic iodides except AgI , Cu_2I_2 , Hg_2I_2 and PbI_2 are soluble in water.

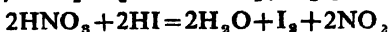
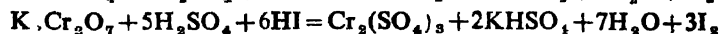
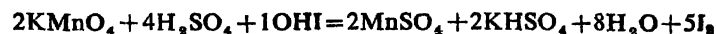
(3) *It is a monobasic acid.* In aqueous solution, it turns blue litmus red and behaves as a strong acid.

Hydroiodic acid on being reacted with many metals gives off

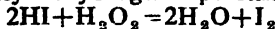
hydrogen. It liberates carbon dioxide from carbonates and reacts with bases to produce salts and water.



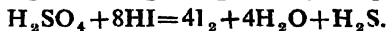
(4) *Hydrogen iodide is a vigorous reducing agent.* It is readily oxidised with liberation of iodine by mild and strong oxidising agents.



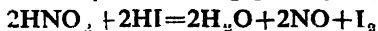
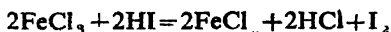
In the above reactions, acidified potassium permanganate, acidified potassium dichromate and nitric acid have been reduced by hydrogen iodide to produce manganous salt, chromic salt and nitrogen dioxide respectively. Hydrogen peroxide undergoes reduction to form water.



Concentrated sulphuric acid gives different reduction products depending on the amount of hydrogen iodide used.



Hydroiodic acid can also reduce ferric salts, cupric salts, nitrous acid etc.



While reducing, hydroiodic acid is oxidised to iodine in each case.

Uses : Hydroiodic acid is used as a reducing agent particularly in organic chemistry.

Tests for hydroiodic acid and metallic iodides :

(1) Hydroiodic acid or a metallic iodide on being heated with concentrated sulphuric acid liberates violet vapours of iodine. Addition of manganese dioxide expedites the action. A piece of paper soaked in starch solution is turned deep blue in contact with the violet vapours.

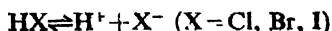
(2) An aqueous solution of hydroiodic acid or an iodide on being treated with chlorine water liberates iodine which dissolves in chloroform or carbon disulphide yielding a violet solution. This solution turns starch solution blue.

(3) When silver nitrate solution is added to an aqueous solution of hydroiodic acid or a metallic iodide, a yellow precipitate of silver iodide is obtained. The precipitate is insoluble in both nitric acid and ammonium hydroxide.

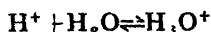
Comparison between hydrogen chloride, hydrogen bromide and hydrogen iodide : These halogen hydric acids display a well marked gradation and similarities in their physical and chemical properties.

(1) Each of these three halogen hydric acids are colourless gases which fume in moist air.

(2) All these compounds are extremely soluble in water and their aqueous solutions behave as strong acids of about the same strength. The solutions in water dissociate as :



In fact, hydrogen ion does not remain simply as H^+ but is present as a hydrated form or the hydroxonium ion $(\text{H}_3\text{O})^+$



The solubility of halogen hydric acids increases from chlorine to iodine as shown below.

	HCl	HBr	HI
Solubility in water at 0°C	42	68	90%

(3) The stability of these acids on the other hand decreases gradually from hydrochloric to hydroiodic acid. Dissociation of hydrogen chloride into hydrogen and the halogen occurs at above 1500°C. Hydrogen bromide undergoes slight dissociation at 800°C whereas hydrogen iodide dissociates considerably at a temperature between 300° and 400°C or even at sunlight

(4) Reducing character of these acids increases with increasing atomic weight of the halogen. Thus, hydroiodic acid possesses remarkable reducing properties. The ease of oxidation of the hydric acids is shown by the reactions with the following oxidants.

Oxidising agent	HCl	HBr	HI
KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, HNO_3	Oxidised to chlorine,	Oxidised to bromine	Oxidised to iodine
H_2SO_4 , H_2O_2	No action	„	„
Solution of cupric and ferric salts, HNO_2	„	No action	„

The reactions with solutions of cupric and ferric salts or with nitrous acid show that HI is more easily oxidised than HBr and HCl.

(5) The solubility of the salts of the above halogen hydracids is to be noted. All halides except halides of silver, lead and mercurous mercury are soluble in water. Cuprous iodide is also insoluble in water. When hydrochloric, hydrobromic or hydroiodic acid is added to aqueous solutions of silver and lead salts, the insoluble chlorides, bromides or iodides of the metals are precipitated.

$\text{AgNO}_3 + \text{HCl} = \text{HNO}_3 + \text{AgCl} \downarrow$ (curdy white precipitate, insoluble in nitric acid but soluble in ammonium hydroxide)

$\text{AgNO}_3 + \text{HBr} = \text{HNO}_3 + \text{AgBr} \downarrow$ (Light yellow precipitate, insoluble in nitric acid but dissolves slowly in ammonium hydroxide.)

$\text{AgNO}_3 + \text{HI} = \text{HNO}_3 + \text{AgI} \downarrow$ (Yellow precipitate, insoluble in both nitric acid and ammonium hydroxide)

$\text{Pb}(\text{NO}_3)_2 + 2\text{HCl} = 2\text{HNO}_3 + \text{PbCl}_2$ (White precipitate, soluble in hot water),

$\text{Pb}(\text{NO}_3)_2 + 2\text{HBr} = 2\text{HNO}_3 + \text{PbBr}_2$ (Precipitate, soluble in hot water),

$\text{Pb}(\text{NO}_3)_2 + 2\text{HI} = 2\text{HNO}_3 + \text{PbI}_2$ (Yellow precipitate, soluble in hot water).

CHAPTER 7

MANUFACTURE OF SOME IMPORTANT CHEMICALS

Manufacture of Ammonia :

On the industrial scale, ammonia is obtained :

- (1) by direct combination of nitrogen and hydrogen by Haber's synthetic process.
- (2) by hydrolysis of calcium cyanamide.
- (3) as byproduct in the manufacture of coal gas.

Haber's synthetic process :

Principle : The large-scale production of ammonia is made by the direct combination of nitrogen and hydrogen at a high pressure and a fixed temperature in presence of a catalyst. The process is based on the following reversible, exothermic reaction.



Conditions for successful operation of the process :

- (1) A mixture of nitrogen and hydrogen in the ratio of 1 : 3 is taken.
- (2) It appears from the equation that the formation of ammonia from its elements is accompanied with a diminution in volume (hence the number of molecules) i.e. 1 volume of nitrogen and 3 volumes of hydrogen react to give 2 vols. of ammonia.

So, according to Le Chatelier's principle, high pressure will favour the production of ammonia. In practice, the working pressure of 200 atmospheres is generally applied in Haber's process. The use of very high pressure is limited by engineering difficulties and the fear of explosion.

- (3) The reaction between nitrogen and hydrogen is exothermic. So, it is evident from Le Chatelier's principle that the low temperature favours the production i.e. the lower the temperature, the greater is the yield of ammonia. Lowering of temperature increases the yield no doubt, but diminishes the speed of the reaction to a great extent. Consequently, it will take a much longer time to obtain an appreciable quantity of ammonia. We know that the time is an important factor in any commercial process. So, it becomes necessary to select a high temperature at which the reaction

proceeds at a workable speed, giving a fairly good yield of ammonia. The temperature thus chosen is known as the optimum temperature. The optimum temperature in this process has been found to be 550°C under a pressure of 200 atmospheres and in presence of a suitable catalyst.

(4) The catalyst employed in Haber's process to hasten the speed of the reaction is the reduced iron powder mixed with a promoter like powdered molybdenum or admixtures of aluminium oxide and potassium oxide.

Nowadays, ferric oxide catalyst with K_2O and Al_2O_3 as promoters is used.

(5) In order to make the reversible reaction proceed in the forward reaction, ammonia formed is removed immediately from the reaction vessel.

(6) As the catalyst is very susceptible to poisoning, the gas-mixture used must be carefully purified and freed from impurities like phosphorus, arsenic, sulphur, dust particles etc

Description of the process : A mixture of pure and dry nitrogen and hydrogen in the volumetric proportion of 1 : 3 is compressed to 200 atmospheres and is admitted into the reaction chamber (catalyst-chamber) which is a upright cylinder made of chrome-vanadium steel. The reacting gases are pre-heated by circulating around the outside of the central cylinder and then passed down the cylinder containing trays of reduced iron (catalyst) and molybdenum powder (promoter). A mixture of alumina and potassium oxide is also used as a promoter. Initially, the catalyst is electrically heated to 550°C . But once the reaction starts, no external heating is necessary as the heat of the reaction is sufficient to maintain the temperature of the catalyst. Nitrogen and hydrogen react in contact with the heated catalyst and are partially converted into ammonia (8–12%).

Collection : The issuing hot gases containing ammonia, unreacted nitrogen and hydrogen are then passed through a spiral

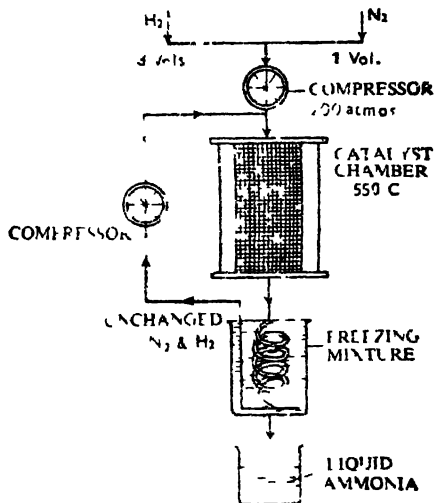


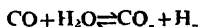
Fig. 2(75) Manufacture of ammonia—Haber's process

tube cooled in freezing mixture when ammonia condenses to a liquid and collects in the vessel kept below. Sometimes, ammonia is removed by absorbing in cold water. The residual unreacted nitrogen and hydrogen together with more reaction mixture are circulated again through the catalyst chamber. Thus, the process is made continuous.

Commercial synthesis of ammonia by Haber's process is conducted in different countries under different pressures and temperatures.

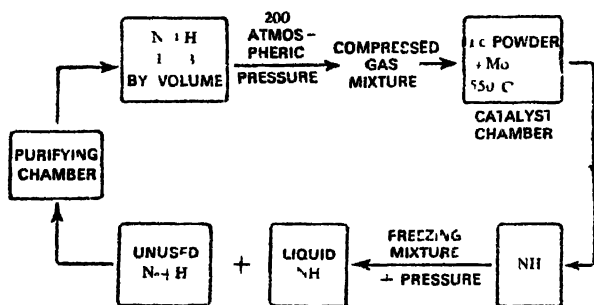
Source of nitrogen and hydrogen required in the process. (1) Nitrogen may be obtained by fractional distillation of liquid air and hydrogen by electrolysis of water. But electrolytic hydrogen cannot be used profitably unless the electricity is cheap and easily available.

(2) The required nitrogen and hydrogen are usually made from producer gas (a mixture of carbon monoxide and nitrogen in the ratio of 1 : 2 by volume obtained by passing air over a bed of red hot coke) and water gas (a mixture of equal volumes of carbon monoxide and hydrogen obtained by passing steam over white hot coke) respectively. The producer gas and water gas are mixed together in such a correct proportion that nitrogen and hydrogen in the final mixture remain in the ratio of 1 : 3 by volume after removal of carbon monoxide. To remove carbon monoxide from the above mixture the gases are mixed with requisite quantity of steam and led over a heated catalyst consisting of a mixture of ferric oxide and chromium oxide at 450°C.



Carbon monoxide is thus converted into carbon dioxide which is removed by absorption in water under pressure. Any residual carbon monoxide is removed by washing with ammoniacal cuprous chloride solution. The gas mixture (N_2 and H_2) is then dried before use.

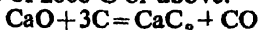
A flow diagram showing the manufacture of ammonia



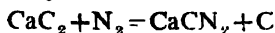
Cyanamide process : The method may be divided into three parts.

(1) Preparation of calcium carbide. (2) Conversion of calcium carbide into calcium cyanamide and (3) Hydrolysis of calcium cyanamide.

Calcium carbide is obtained by heating a mixture of 3 parts by weight of lime and 2 parts by weight of coke in an electric furnace at a temperature of 2000°C or above.

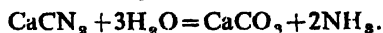


Heated calcium carbide (1100°C approximately) absorbs nitrogen producing calcium cyanamide.



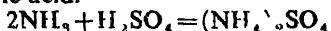
After cooling, cold water is sprayed over the products to decompose any unreacted carbide into calcium hydroxide and acetylene.

Ammonia is liberated by hydrolysing the calcium cyanamide in autoclaves by means of super heated steam under high pressure.



Ammonia from destructive distillation of coal : An important commercial source of ammonia is the ammoniacal liquor obtained as a byproduct in the manufacture of coal gas. This has been described later in this chapter in connection with the manufacture of coal gas and its byproducts.

Conversion of ammonia into ammonium sulphate : (a) A solution of ammonium sulphate may be obtained by directly absorbing ammonia prepared by Haber's process or from coal gas works into dilute sulphuric acid.



The solution on evaporation and cooling separates crystals of ammonium sulphate which are dried by means of a centrifuge.

This method of production of ammonium sulphate requires sulphuric acid. So, the countries where the acid is made commercially at a cheap rate (i.e. where sulphur is less costly and easily available) can only meet the requirements of ammonium sulphate by this process.

(b) Ammonia may be readily converted into ammonium sulphate by passing it together with carbon dioxide into a well-stirred suspension of finely crushed calcium sulphate (or mineral gypsum $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$) in water. Insoluble calcium carbonate and soluble ammonium sulphate are formed as a result of the reaction.



The precipitated calcium carbonate filtered off and the filtrate left is an aqueous solution of ammonium sulphate. It is evaporated and cooled, when crystals of ammonium sulphate are obtained.

Ammonium sulphate is a very important nitrogenous fertilizer. The Sindri Fertilizer Project in Bihar utilises the above method for the production of ammonium sulphate.

Conversion of ammonia into Urea.

Urea, an important nitrogenous fertilizer, is nowadays manufactured from ammonia.

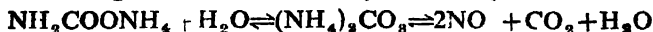
Urea is obtained by heating anhydrous liquid ammonia and liquid carbon dioxide at 150°C under a pressure of 200 atmospheres. Traces of moisture catalyse the reaction. The reaction is carried out in a special type of closed vessel called 'autoclave'.

The reaction takes place in two stages. At first, ammonium carbamate is produced by the interaction of ammonia and carbon-dioxide. The carbamate is then decomposes to yield urea and water.



The yield of urea is improved if ammonia is taken in excess. Generally, ammonia and carbon dioxide are taken in the molecular proportion of 3 : 1.

After the reaction, the products are dissolved in water and distilled carefully when unreacted gases and ammonium carbamate are removed. Ammonium carbamate on being hydrolysed produces ammonium carbonate which decomposes into ammonia and carbon dioxide. The gases thus evolved may be used again



The urea remaining in solution is separated by crystallization or by evaporating the water by spraying.

MANUFACTURE OF NITRIC ACID

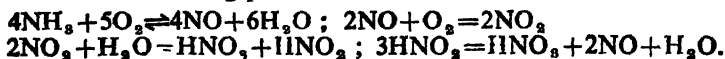
Nitric acid is manufactured by three methods :

- (1) Catalytic oxidation of ammonia—Ostwald process.
- (2) By the combination of nitrogen and oxygen of the air—Barkeland-Eyde process.
- (3) Distillation of Chile-saltpetre with concentrated sulphuric acid.

(1) **Catalytic oxidation of ammonia —Ostwald process :** On an industrial scale, nitric acid is now extensively made by this process.

Principle : In this process, a mixture of synthetic ammonia obtained by Haber's process and excess of air is passed for a short time over platinum gauze catalyst heated to 750—900 C when ammonia is oxidised by atmospheric oxygen into nitric oxide. This is a reversible, exothermic reaction and is regarded as the main reaction of Ostwald method. The nitric oxide thus produced is oxidised by more air to nitrogen dioxide and the dioxide when treated with water produces nitric acid.

The reactions taking place are :



The nitric oxide liberated at the end of the process is reoxidised by the air present giving nitrogen dioxide which goes through the same cycle of reactions.

Procedure : Air taking part in the oxidation is preheated to about 500°C in a heat exchanger by means of hot gases issuing from the converter and is freed from the dust particles by filtering through cotton wool in the air-filter. A mixture of pure, dry

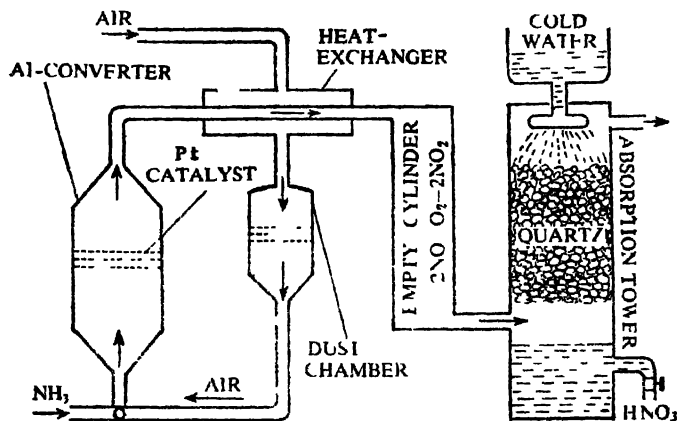


Fig. 2(76)—Ostwald process of manufacture of nitric acid

ammonia and preheated air (in the proportion of 1 : 7.5 by volume) is admitted into an aluminium box called converter across the middle of which several screens of platinum wire gauze catalyst are fixed. The gas mixture is forced to pass through the converter so rapidly that the period of contact with the catalyst does not exceed 0.03 second. The platinum catalyst is initially heated electrically to a temperature of 750°C to start the reaction and subsequently, the heat produced by the exothermic reaction (oxidation of ammonia) maintains the temperature of the catalyst at that point. The hot products are passed through the heat interchanger to heat the incoming air and the process goes on without external heating.

About 90 percent or more of ammonia is oxidised to nitric oxide. Steam is also formed as one of the products. The hot gases leaving the converter are nitric oxide, steam, excess of air and unchanged ammonia. These gases are cooled to about 50°C by passing through a heat-interchanger where they transfer some of their heat to the incoming air and is admitted into an empty aluminium cylinder. Here, nitric oxide is oxidised to nitrogen dioxide by the accompanying air. The dioxide then passes up a stainless steel absorption tower packed with broken pieces of quartz over which water flows from above. Nitrogen dioxide reacts with water producing nitric acid solution (about 50%) which is collected from the bottom of the tower.

In actual practice, a series of absorption towers is employed for the collection of dilute acid which is then concentrated.

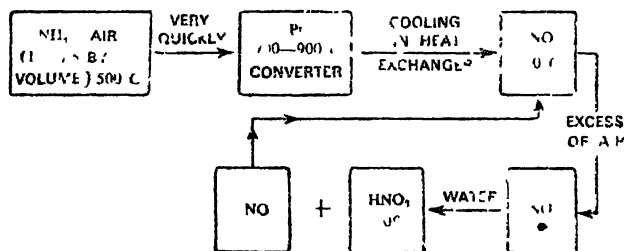
In connection with this method, the following important points are to be remembered.

(1) The reaction mixture (ammonia and air) must be very rapidly passed through the converter so that the time of contact of the gases with the platinum gauze catalyst is very short as otherwise ammonia is oxidised to nitrogen instead of nitric oxide. $4\text{NH}_3 + 3\text{O}_2 = \text{N}_2 + 6\text{H}_2\text{O}$; $4\text{NH}_3 + 6\text{NO} = 5\text{N}_2 + 6\text{H}_2\text{O}$

(2) The gases must be pure and be freed from dust particles because such impurities poison the catalyst.

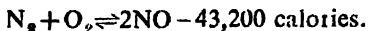
(3) Nowadays, the reactions are conducted at a pressure of 7 to 8 atmospheres and platinum-rhodium gauze is employed as the catalyst.

A flow diagram showing the manufacture of nitric acid by Ostwald process :



(2) **By direct combination of atmospheric nitrogen and oxygen —Birkeland and Eyde process :** In this process, the atmospheric nitrogen and oxygen are used as the raw materials for the production of nitric acid on commercial scale. The process is very costly due to the consumption of high electrical energy to produce the high temperature at which the combination of nitrogen and oxygen occurs. The process is now obsolete and has completely been replaced by Ostwald process. So, only the principle of the method is given here without going into the details.

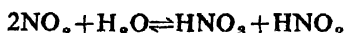
When nitrogen and oxygen of the air are heated at a high temperature of 3000 C produced by means of an electric spark, the two gases combine to give nitric oxide.



It is a reversible, endothermic reaction. So according to Le Chatelier's principle, high temperature favours the production of nitric oxide. It is clear that numbers of molecules are equal on both sides of the equation and hence the yield will remain unaffected by a change of pressure

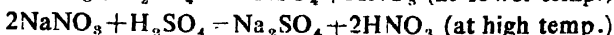
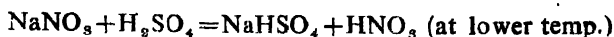
The nitric oxide formed and the air are rapidly cooled, when nitric oxide reacts with the oxygen of the air yielding nitrogen peroxide or dioxide. $2\text{NO} + \text{O}_2 = 2\text{NO}_2$

The dioxide when dissolved in cold water is converted into nitric acid.



(3) **By distilling Chile saltpetre with concentrated sulphuric acid :** This process of manufacturing nitric acid is similar to that used in the laboratory method of preparation. Costly potassium nitrate is only replaced by cheap sodium nitrate which is obtained in great quantities from the nitre beds of Chile.

Principle : Sodium nitrate (Chile saltpetre) on being heated with concentrated sulphuric acid yields nitric acid. The reaction takes place in two stages.



Total reaction, $3\text{NaNO}_3 + 2\text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{Na}_2\text{SO}_4 + 3\text{HNO}_3$

Description of the process : Chile saltpetre and concentrated sulphuric acid (in 3 : 2 molar proportion) are taken in a large cast iron retort set in a brickwork furnace.

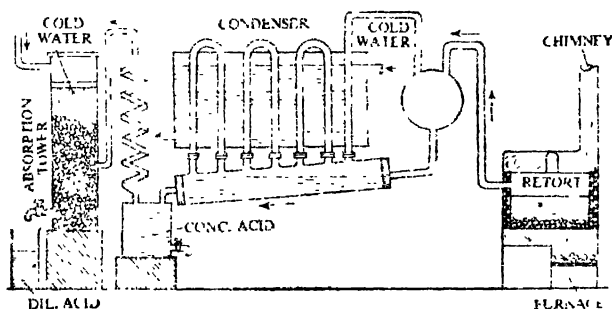


Fig. 2(77)—Manufacture of nitric acid from Chile salt petre

By means of coal fire, the retort is uniformly heated to about 200—250°C so that the nitric acid formed inside remains completely in the vaporous state. Nitric acid vapours do not attack the iron retort. The vapours of the acid escape through the outlet of the retort and enter into the cooling chamber having a series of water-cooled earthenware or silica pipes connected together. These pipes are acid-resistant and serve as the condensers. The nitric acid vapours leaving the retort condense in these pipes and collect in the stoneware receivers as concentrated nitric acid.

The uncondensed vapours are then made to pass up a tower packed with stoneware balls down which a stream of water flows. Here, nitric acid vapours and the vapours of nitrogen dioxide (produced by the decomposition of a part of nitric acid during distillation) dissolve in water giving dilute nitric acid.

This method is easy to carry out and is employed for the large scale production of nitric acid in India.

MANUFACTURE OF SULPHURIC ACID

Two methods are in use for the manufacture of sulphuric acid—(1) The contact process and (2) The Lead chamber process. Both the processes are based on the catalytic oxidation of sulphur dioxide.

The Lead chamber process has not been included in the syllabus of W.B.H.S. Council and is not discussed here. But the students should remember that the reactions involved in the chamber process are similar to those taking place in the laboratory method of preparation. The acid produced by this process is of 60–65% strength. In the contact process, we get 98% sulphuric acid or sometimes 100% pure acid.

Contact Process :

Principle : When a mixture of pure, dry sulphur dioxide and excess of air is passed over a heated solid catalyst like finely powdered platinum, platinised asbestos or vanadium pentoxide (V_2O_5), sulphur dioxide gets oxidised by the oxygen of the air into sulphur trioxide which on being reacted with water yields sulphuric acid.



But in actual practice, sulphur trioxide is not dissolved in water directly but is absorbed in concentrated sulphuric acid. The resulting fuming sulphuric acid or oleum chemically known as pyrosulphuric acid is cautiously diluted with water to give 98% sulphuric acid or sometimes 100% pure acid,

The favourable conditions of the process :

(1) The most important condition for the successful operation of the process is that the mixture of sulphur dioxide and air used must be completely freed from dust particles, sulphur, arsenious oxide, hydrogen sulphide, water vapour etc. These impurities poison the catalyst and the reaction is ultimately stopped. The activity of the solid catalyst is much enhanced if it is used in a finely divided form providing greater surface of contact.

(2) The oxidation of sulphur dioxide is an exothermic, reversible reaction. $2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45.2 \text{ Cals.}$

If K be the equilibrium constant, then according to the law of mass action

$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 \times [\text{O}_2]}$$

Since the value of K is fixed, the use of excess of oxygen (air) favours the conversion of more sulphur dioxide into sulphur trioxide.

(3) The reaction is exothermic. So, according to Le Chatelier's principle, the yield of sulphur trioxide is greater when the working temperature is lower. But lowering of temperature reduces the reaction rate to a great extent and it will require a much longer period of time to obtain an appreciable quantity of sulphur trioxide.

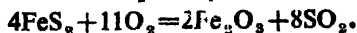
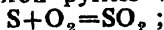
Thus, the above conversion at low temperatures is not advantageous in an industrial process. In contact process, the oxidation reaction is conducted in presence of finely divided platinum or vanadium pentoxide catalyst at a temperature of 450°C (optimum) at which the rate of reaction is not too slow and the yield of sulphur trioxide is fairly good.

(4) It appears from the equation that the reaction is accompanied by a decrease in volume or number of molecules. Therefore, Le Chatelier's principle demands that the use of high pressure will improve the yield. But if the conversion is made at the above working conditions, the increase of pressure makes no appreciable improvement of yield. Hence, in industry, the process is worked at 1.5 atmospheres.

(5) If the product (SO_3) is removed from the sphere of action as soon as it is formed, more and more reactants will combine to form sulphur trioxide.

(6) When sulphur trioxide is passed into water, only a slight amount of it dissolves in water. The heat produced during the direct absorption of sulphur trioxide in water leads to the formation of fine mist of the acid which cannot be condensed. So, it is absorbed in 98% sulphuric acid.

Description of the process : (A) Production of sulphur dioxide : The most important raw material sulphur dioxide is produced by burning sulphur or iron pyrites with excess of air in a special burner.



The gas mixture leaving the burner contains 8% of sulphur dioxide, 82% of nitrogen and 10% of oxygen.

(B) Purification of the gas mixture : The mixture of sulphur dioxide and excess of air from the sulphur burner is carefully purified by passing through a dust or steam chamber where the

particles of dust, sulphur, arsenious oxide and other suspended materials are made to settle down by injecting steam on them. The gas mixture thus purified is cooled to about 100°C by passing through a spiral lead pipe and is admitted through the bottom of a tower containing earthen ware balls where the mixture meets a spray of water which dissolves the soluble impurities. The issuing moist gases are then dried by passage through another tower (scrubber) packed with coke down which concentrated sulphuric acid is allowed to percolate. The gases are washed by

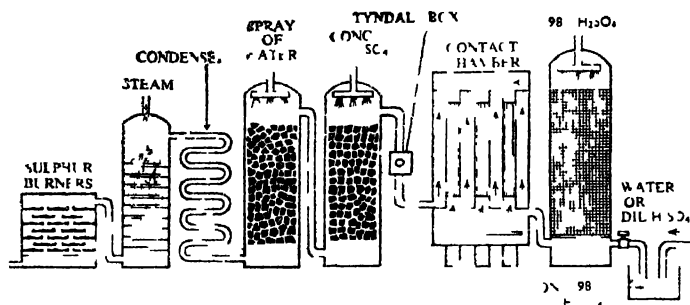


Fig 2 78) Manufacture of sulphuric acid by contact process

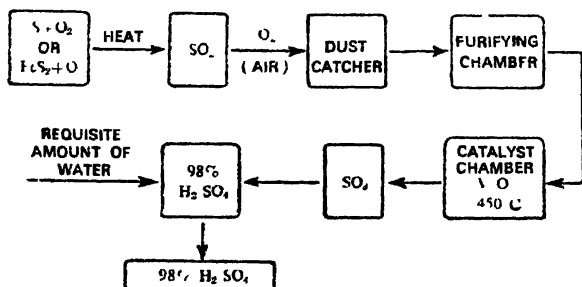
the acid and is freed from the moisture. The pure and dry gas mixture appears to be transparent. The transparency is examined in a glass box (Tyndall box) in a beam of powerful light. When no suspended particle is present, the gases are passed into the contact chamber or reaction chamber made of iron.

(C) Oxidation of sulphur dioxide. The contact furnace or chamber contains a few vertical iron tubes packed with the powdered catalyst (platinised asbestos) and heated externally to about 500°C at the start. The incoming gas mixture first circulates round the hot tubes whereby the pipes lose a part of their heat and the mixture is preheated. The preheated mixture now passes down the contact pipes in which sulphur dioxide is oxidised into sulphur trioxide with evolution of much heat. The passage of the cold reacting gases into the contact chamber is controlled in such a way that the temperature of the catalyst is maintained at 450°C (optimum temp). Since the oxidation reaction is exothermic, no further heating is necessary after the reaction has once started.

(D) Absorption of sulphur trioxide.—Collection of sulphuric acid. Sulphur trioxide leaving the contact chamber is passed through a heat exchanger (not shown in the fig) and the gas thus cooled is absorbed in 98 percent sulphuric acid in an absorbing tower forming fuming sulphuric acid which collects in a tank,

A stream of water or dilute acid is allowed to run into the tank in such a controlled way that the strength of the acid is always maintained at 98 per cent.

A flow diagram of manufacture of sulphuric acid by Contact process :

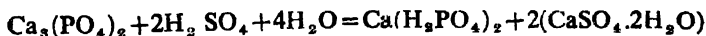


Fuming sulphuric acid or oleum. On passing excess of sulphur trioxide into 98% sulphuric acid, an oily fuming liquid is obtained. This is known as fuming sulphuric acid or oleum. Oleum, on dilution with requisite amount of water, yields 100 percent sulphuric acid or sulphuric acid of different strengths.

SUPER PHOSPHATE OF LIME

To increase the fertility of the soil, the use of artificial fertilizers containing phosphorus is a regular necessity. Natural phosphorus compounds phosphorites, apatites etc. and the animal bones contain phosphorus in the form of insoluble tertiary phosphate, $\text{Ca}_3(\text{PO}_4)_2$. Due to its insolubility in water, this mineral tricalcium phosphate is unsuitable for use as a fertilizer. Readily soluble phosphates to be used as quick-acting fertilizers are obtained from these insoluble phosphatic minerals by chemical treatment. Super-phosphate is the name given to a soluble phosphatic fertilizer.

Preparation : Powdered mineral phosphate such as phosphorite or apatite is treated with calculated amount of sulphuric acid (60–70%) when the insoluble normal tricalcium phosphate is converted into the soluble primary monocalcium phosphate. Hydrated calcium sulphate is also formed as one of the products.



The mixture consisting of monocalcium phosphate (or calcium dihydrogen phosphate) and calcium sulphate (gypsum) is known as *super phosphate of lime*.

Description of the process : Equal quantities of finely ground mineral phosphate and sulphuric acid (chamber acid containing 60–70% H_2SO_4) are run into a cast iron mixer provided with

revolving blades. The mixture is stirred for two to five minutes.

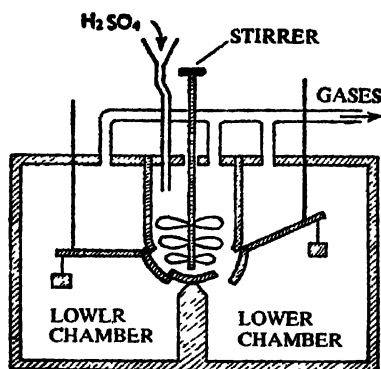


Fig. 2(79)—Preparation of super phosphate of lime

and then discharged quickly through the outlet into the brick-lined pits or dens below. The pits when half filled are closed for 24–48 hours for completion of the reaction which starts in the mixer. The reaction takes place with rise of temperature to 100°C and with evolution of various gases like carbon dioxide, silicon tetra-fluoride, hydrogen chloride etc. which are absorbed in absorption towers. The evolved gases give porosity to the material. After the reaction, the whole mass stiffens. Super phosphate of lime is then taken out, carefully

dried by hot air and broken into fine grains for use.

COAL GAS

Composition of coal gas : Coal gas which consists essentially of a mixture of hydrogen, methane, carbon monoxide, ethylene, acetylene, benzene vapour, nitrogen, carbon dioxide, oxygen etc. is used as a fuel and for illuminating purposes.

Coal, on being subjected to destructive distillation, gives rise to both volatile and non-volatile products. When the volatile matter is cooled, a portion of it condenses to liquid. The remaining gaseous portion which escapes condensation is known as *coal gas*. The composition of coal gas varies with the nature of the coal used and the temperature of distillation.

The gaseous constituents of the coal gas fall into three groups. An approximate percentage composition of coal gas by volume is given below.

- | | | | |
|---|---|--|--------|
| (1) Heat producing but non-illuminating | { | Hydrogen | 45–50% |
| | | Methane | 25–35% |
| | | Carbon monoxide | 5–11% |
| (2) Illuminants—light producing | { | Ethylene, acetylene and benzene vapour | 2.5–5% |
| (3) Inert diluents : | { | Nitrogen | 2–10% |
| | | Carbon dioxide | 0–0.3% |
| | | Oxygen | 0–1.5% |

Besides, H_2S and some other substances may remain as impurities.

Manufacture of coal gas : Coal gas is manufactured by the destructive distillation of coal.

Powdered soft or bituminous coal is taken in a row of horizontal (or vertical) air-tight retorts made of fireclay. The retorts are externally heated to about $1000-1200^{\circ}\text{C}$ by means of producer gas burning in air when coal gets decomposed into an enormous variety of products. The volatile products given off rise up from the retorts through the vertical iron ascension pipes leading into a horizontal main known as hydraulic main containing water at a fixed level. Here, the temperature of the gas mixture falls to about 60°C and a portion of it condenses into tar and water having dissolved ammonia and some ammonium salts. The excess of the condensed liquid (tar, water etc.) flows into the tar-well below. The hot gas mixture issuing from the hydraulic main passes in succession through a series of air (or water) cooled vertical iron pipes acting as condensers. The gas is further cooled here and is condensed to form more liquid which runs into the tar-well. The liquid in the storage well separates into two layers—(a) the upper watery layer being ammoniacal liquor or gas liquor which contains free ammonia and ammonium salts and (b) the lower tarry layer called coal tar containing a vast number of hydrocarbons. With the help of suction pumps, the coal gas (containing impurities like NH_3 , HCN , CO_2 , H_2S , CS_2 etc. is drawn out of the condensers and is forced to enter into a long iron tower (called washer or scrubber) packed with coke. Down this tower flows a stream of water while the gas passes up. All traces of ammonia, tar and some hydrogen cyanide, carbon dioxide, hydrogen sulphide are washed away with water in the scrubber. The gas thus washed still contains hydrogen sulphide, carbon disulphide, carbon dioxide and hydrogen cyanide as impurities, the presence of which being highly objectionable in a gaseous fuel. To remove these impurities, the gas is led through the purifiers which are rectangular iron tanks fitted

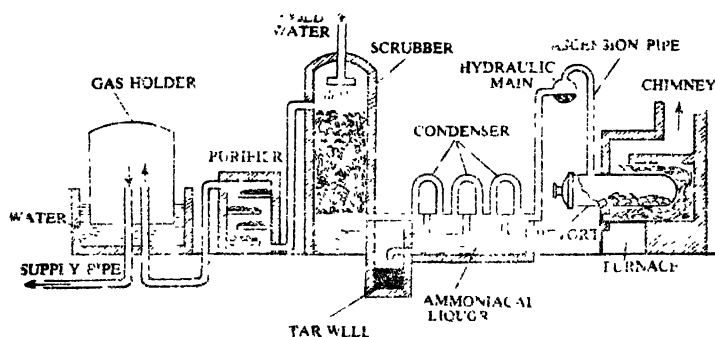
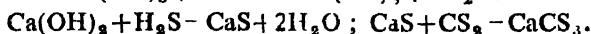
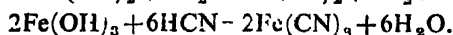
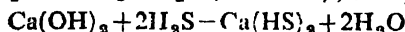
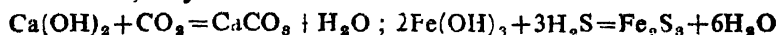


Fig. 2.80)—Manufacture of coal gas

with horizontal shelves on which hydrated ferric oxide (ferric hydroxide) is spread. On some of the shelves, slaked lime is also placed. In the purifiers, all CO_2 and some H_2S , HCN , CS_2 are

absorbed in slaked lime and removed. Moist ferric oxide absorbs the last traces of H_2S , and HCN .

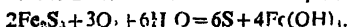
Actually, any of the absorbing agents (hydrated ferric oxide or slaked lime) may be used.



The coal gas, thus purified is finally stored over water in big gas-holders.

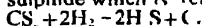
The solid substance left in the retorts after the destructive distillation of coal is coke. A hard dense deposit of carbon formed due to the thermal decomposition of hydrocarbons is found on the inner walls of the retorts. This is gas carbon.

Hydrated ferric oxide on being reacted with hydrogen sulphide is converted into ferric sulphide and loses its absorbing power. It is then called spent oxide of iron. The iron oxide, thus exhausted, is exposed to the air, whereby hydrated oxide is regenerated and can be used over again. Free sulphur is also separated. Spent oxide is utilised as a source of sulphur

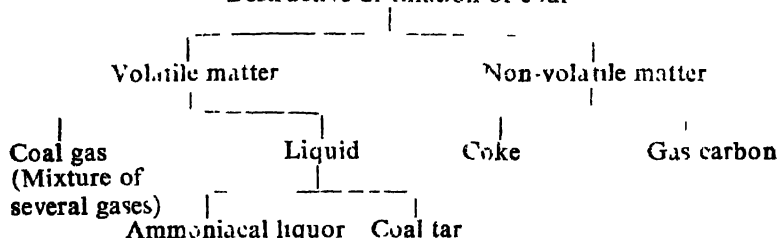


The used-up lime in the purifiers forms spent lime or gas lime.

It is very difficult to remove carbon dioxide completely from the gas mixture. For its complete removal, the coal gas in some gas works is passed over nickel heated to 450°C . Carbon disulphide and hydrogen present in the gas react together forming hydrogen sulphide which is removed as usual by hydrated ferric oxide.



Destructive distillation of coal



Byproducts of coal gas industry—their uses :

(1) **Coal tar** : Coal tar is a dark black, foul-smelling viscid liquid but is a mixture of a large number of valuable organic compounds. When subjected to fractional distillation, it gives rise to benzene, toluene, naphthalene, anthracene, phenol and many other important substances which are the starting materials for various dyes, drugs, perfumes and explosives. Besides, it is used for preserving timbers, in preparing water-proof gunny bags and for protecting iron from rusting. The 'pitch' which is left after distillation is used for road making. Mixed with oil, it is used in making varnishes.

(2) **Ammoniacal liquor** : It is an aqueous solution of ammonia, ammonium salts like ammonium carbonate, ammonium hydro-sulphide etc. On boiling with excess of milk of lime, it produces gaseous ammonia which can be directly absorbed in sulphuric acid to give ammonium sulphate, a very important nitrogenous fertilizer. Ammonia gas when passed into water gives liquor ammonia of commerce.

(3) **Spent oxide of iron** This is obtained from the purifiers. It is employed as a source of sulphur which when burnt in air gives sulphur dioxide required in the commercial production of sulphuric acid. It is also used in the manufacture of potassium ferrocyanide.

(4) **Spent lime or gas lime** : It is obtained from the purifiers and is used as a manure.

(5) **Gas carbon** It is a good conductor of heat and electricity and widely used in making electrodes.

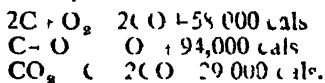
(6) **Coke** Coke is extensively used as a good fuel and in wet blurgy as a reducing agent. It is also used in the manufacture of water gas and producer gas.

N.B. The destructive distillation of coal is also known as carbonisation of coal. The nature and quantity of the products depend largely on the temperature of distillation. The distillation of coal at low temperature (600–650°C) is called low temperature carbonisation and when the distillation is carried out at high temperature (1000–1200°C), it is called high temperature carbonisation. In either case, coal gas, coal tar and coke are the main products but the products of the two processes differ in quantity as well as in quality.

Coal when subjected to low temperature carbonisation gives much less coal gas. But the gas is of high calorific value and is a better fuel. The low temperature process yields a coal tar which contains large amounts of naphthalene and paraffin hydrocarbons. This tar on distillation gives motor spirit. Moreover, this process gives a coke which is soft and easily inflammable and burns without smoke. This is why it is used as a fuel in glass making. It is also obtained from the high temperature carbonisation of coal. The high temperature coke is hard and burns with smoke. It is used as a reducing agent and a fuel in metallurgical industries.

* Other important gaseous fuels :

Producer gas Producer gas is essentially a mixture of carbon monoxide and nitrogen and is a cheap industrial fuel. Some carbon dioxide is also present in the mixture. It is prepared by passing a regulated supply of air through a bed of red hot coke (temperature 1000°C) in a special kind of furnace called producer.



The formation of producer gas is accompanied with the evolution of large amounts of heat which is carried away by the gas. With a view to saving the loss of this heat, the producer gas fresh

* Not included in the W. B. H. S. Syllabus.

from the generating plant is mixed with air and burnt so that the heat liberated during the formation is added to that generated as a result of combustion.



The gas generating plant or producer is simply a large air-tight stove. Suitable arrangements for admitting the fuel and removing the ash without disturbing the process are also provided.

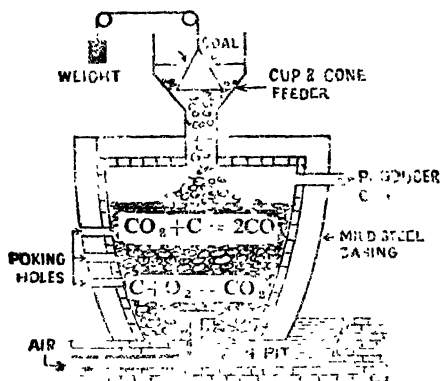


Fig. 2(81) Producer gas generator

The fuel is fed from the top by a cup and cone arrangement. The producer is provided at the base with an inlet through which air is introduced. The gas leaves the plant through a gas outlet.

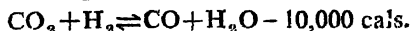
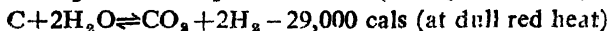
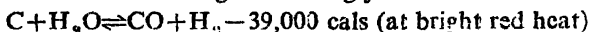
Its average percentage composition by volume is
 $\text{CO}, 20; \text{N}_2, 60;$

$\text{CO}_2, 6$ and $\text{H}_2, 8$

Producer gas is used in

heating coal gas retorts and metallurgical furnaces.

Water gas : Water gas is a mixture consisting of about equal volumes of hydrogen and carbon monoxide. It is obtained by passing steam into a bed of white hot coke (temp. $1000^\circ\text{--}1400^\circ\text{C}$). A little carbon dioxide remains in the gas. The reaction involved in the formation of water gas is strongly endothermic.



Water gas is a valuable fuel having a high calorific value. It is used in the manufacture of hydrogen, methyl alcohol and synthetic petrol. It is also employed as a reducing agent in metallurgy.

QUESTIONS

FIRST PAPER — Group A

CHAPTER 1 : Introduction

1. What is chemistry? What are the different branches of chemistry? Justify the statement—"Chemistry is an experimental science."

2. Define and illustrate (a) Element, (b) Compound, (c) Mixture, (d) Exothermic and endothermic compounds.

3. Tabulate the essential differences between a mixture and a chemical compound of iron and sulphur.

It is stated that a heterogeneous substance must be a mixture. Is the converse that a mixture must always be heterogeneous true? Justify your answer with suitable examples.

4. State with reasons which of the following are elements, compound and mixtures :

Water, Sugar, A mixture of common salt, Iron powder, Carbon, Nitrogen, Petroleum sulphur, Brass, Clay powder, Rust, Air, Aerated water, Milk, Kerosene oil.

CHAPTER 2 : Law of chemical combination — Dalton's atomic theory

I

1. What do you mean by a law, hypothesis and theory? Distinguish between a law and a hypothesis.

2. State and explain with suitable examples the laws of chemical combination by weight and by volume.

How are these laws deduced from Dalton's atomic theory?

3. Lavoisier enunciated a fundamental law of chemical combination. State and explain the law. How will you explain this law in the light of Dalton's atomic theory?

Describe a suitable experiment by means of which you can verify the law.

4. State the law of conservation of mass. How would you reconcile the following facts with the law just mentioned.

(a) A candle burns in open air and loses in weight. (b) A piece of camphor left exposed in air loses in weight. (c) Magnesium burns in air and gains in weight. (d) A piece of iron on exposure to moist air increases in weight. (f) A piece of charcoal when ignited burns away leaving a small quantity of ash behind.

5. Show that the following phenomena are not in contradiction to the law of conservation of mass.

(a) A piece of copper when strongly heated in air gains in weight.

(b) Copper carbonate, if heated, loses in weight.

(c) A naphthalene ball kept on a watch glass disappears gradually.

In the strictest sense, the law of conservation of mass is admitted to be inexact in many chemical changes accompanied by evolution of much energy (heat), but the law holds good for ordinary chemical reactions. Criticise the statement.

6. State and explain the law of constant or definite proportions. Show, with one example, that the converse statement is not always true.

7. State the law of multiple proportions. Verify the law using the compounds of carbon and oxygen.

The composition of the oxides of nitrogen illustrates the law stated. The law of definite proportions and the law of multiple proportions are not always free from defects. Discuss.

8. State the law of reciprocal proportions and illustrate it with two examples. Why is the law of reciprocal proportions also called law of equivalent proportions?

9. Define an atom according to Dalton. State the fundamental postulates of Dalton's atomic theory. How are the law of conservation of mass, law of multiple proportions and the law of reciprocal proportions explained in the light of the theory? How does present day atom differ from Daltonian atom?

10. Write notes on : (a) Atom, (b) Molecule, (c) Atomic weight, (d) Gram-atom. What do you understand by the statement : "The atomic weight of chlorine is 35.46." What is the modern unit used in comparing the atomic weights of elements?

11. What is atomic mass unit (a. m. u.)?

The atomic weight of oxygen is 16. How would you calculate the weight of one atom of oxygen in gram? Hence calculate the value of 1 a. m. u.

12. State and illustrate Gay Lussac's law of gaseous volume. In what respect does the law differ from other laws of chemical combination? Can you explain the law on the basis of Dalton's atomic theory?

II

1. Show that the following figures are in accordance with the law of constant proportions :

(i) The solution obtained by dissolving 1 gm. of copper in nitric acid was evaporated slowly to dryness and the solid residue left on strongly heating gave 1.252 gms. of cupric oxide.

(ii) 1.375 gms. of cupric oxide when strongly heated in a current of hydrogen gave 1.098 gms. of metallic copper.

2. Sodium chloride derived from three different sources gave the following results on analysis.

(i) 1.6 gms of sodium chloride contained 0.970 gms. of chlorine.

(ii) 5 gms. of sodium chloride contained 3.034 gms. of chlorine.

(iii) 2.65 gms. of sodium chloride contained 1.608 gms. of chlorine. Which of the laws of chemical combination is illustrated by these figures ?

3. (a) Pure silver chloride on analysis was found to contain 75.26% of silver. Admitting the law of definite proportions, calculate the weight of silver required to produce 15 gms. of silver chloride.
[Ans. 11.289 gms.]

(b) Copper sulphate crystals contain 25.45% of copper and 36.07% of water. If the law of constant proportions is true how much copper should be used to produce 8.316 gms. of the crystals and how much water will they contain ?

[Ans. Copper = 2.116 gms ; water = 2.999 gms.]

4. (a) Given that (i) 0.12 gm. of a metal gives 0.20 gm. of oxide when heated in air (ii) its carbonate and nitrate contain 28.5% and 16.2% of the metal respectively. Apply the law of definite proportions to calculate what weight of the oxide will be obtained by heating 1.00 gm. of each of the carbonate and nitrate.

[Ans. from carbonate 0.475 gm. and from nitrate 0.270 gm.]

(b) Ferrous sulphide contains 36.47 per cent of sulphur. When 1 gm of iron is heated with 2 gms. of sulphur, how much ferrous sulphide is formed and how much sulphur remains unchanged.

[Ans. FeS = 1.574g. S = 1.426g]

5. Two elements A and B combine chemically to form three different compounds. The element B is present in these compounds to the extent of 25%, 14.28% and 7.69%, respectively. Show that these experimental results support a fundamental law of chemistry. State the law.

6. Analytical results show that (a) Three binary compounds of nitrogen and hydrogen contain 17.65%, 12.5% and 2.33% of hydrogen (by weight) respectively.

(b) Two oxides of nitrogen contain 63.65% and 46.68% of nitrogen (by weight) respectively.

(c) Two hydrocarbons contain 75% and 80% carbon respectively.

(d) Two chlorides of a metal contain 35.9% and 52.8% of chlorine respectively.

Show that these results are in agreement with a law of chemical combination.

7. Four oxides of lead contain the following weights of the elements

	Lead	Oxygen
(a) Lead suboxide	5.108	0.20
(b) Lead monoxide	1.2975	0.10
(c) Lead sesquioxide	6.5008	0.75
(d) Lead peroxide	8.110	1.2525

Show that these figures illustrate the law of multiple proportions.

8. 0.5 gm and 0.4 gm of two oxides of a metal gave on reduction by hydrogen 0.1687 gm and 0.100 gm of water respectively. Show that the results illustrate the law of multiple proportions.

9. Three oxides of iron have the following composition

	Iron	Oxygen
(a)	77.78	22.22
(b)	70.00	30.00
(c)	72.42	27.58

Show how they illustrate the law of multiple proportions

10. 1.0 gm of copper was dissolved in nitric acid and on ignition gave 1.25 gms of cupric oxide. 1.00 gm of cuprous oxide when ignited in a current of hydrogen gave 0.563 gm of copper. Show that these results illustrate the law of multiple proportions.

11. The following results were obtained by heating different oxides of lead in a current of hydrogen

- (a) 1.393 gms. of litharge gave 1.293 gms of lead
- (b) 2.173 gm of lead peroxide gave 1.882 gms of lead
- (c) 1.721 gms of red lead gave 1.52 gms of lead

Show that these results are in accordance with the law of multiple proportions

12. Three oxides *a*, *b* and *c* of a certain metal were heated to constant weight in a current of hydrogen and water obtained in each case was weighed. The following results were recorded: (i) *a* gave 8.07% (ii) *b* gave 11.68 and (iii) *c* gave 15.05% of water. Show that the results illustrate the law of multiple proportions.

13. Results of analysis of three different compounds are as follows

Methane	Carbon monoxide	Water
C=75%	C=42.86	H=11.11%
H=25%	O=57.14%	O=88.89%

Show that these results prove the truth of one of the laws of chemical combination.

14. Nitric oxide contains 46.67% nitrogen and 53.33% oxygen. Water contains 11.21% hydrogen and 88.79% oxygen. Ammonia contains 17.78% hydrogen and 82.22% nitrogen. Show that the law of reciprocal proportions is observed in the formation of these compounds.

15. Hydrogen sulphide contains 5.85% hydrogen and 94.15% sulphur. Water contains 11.11% hydrogen and 88.89% oxygen, sulphur dioxide contains 50% sulphur and 50% oxygen.

Which of the laws of chemical combination is illustrated by these results?

16. Results of three experiments are described below :

(i) 0.12 gm. of magnesium produces 0.20 gm. of its oxide ;

(ii) 560 cc. of hydrogen are liberated when 0.6 gm. of magnesium reacts with an acid. (Vol. of H_2 is measured at S.T.P.)

(iii) 0.63 gm. of water is produced from 0.56 gm. of oxygen.

Which of the laws of chemical combination explains these observations? Explain your answer and state the law.

17. (a) Is it possible to find out the atomic weight of the element 'X' from the following data?

85 gms. of the compound XNO_2 contains 32 gms. of oxygen and 14 gms. of nitrogen (atomic weight of nitrogen = 14.0).

(b) If 100 c.c. of hydrogen be allowed to react with 150 c.c. of chlorine at S.T.P. What will be the volume of hydrogen chloride produced? What volume of chlorine will remain as residue?

CHAPTER 3 Avogadro's hypothesis and Molecular theory

I

1. State and illustrate the law of chemical combination which can be explained with the help of Dalton's atomic theory. Show how this law led to the distinction between an atom and a molecule.

2. State the hypothesis which helped in harmonising Gay-Lussac's law of gaseous volume, with Dalton's atomic theory. Give a brief account of the usefulness of the hypothesis in chemistry.

3. State and explain with illustration, Avogadro's hypothesis. Show how it explains Gay-Lussac's law of gaseous volume. How would you prove with this hypothesis that if the vapor density of a substance be 22.0, its molecular weight would be 44.0?

4. What led to the adoption of Avogadro's hypothesis?

Show how this hypothesis modifies Dalton's atomic theory.

5. "Equal volumes of all gases at the same temperature and pressure contain the same number of atoms." Show that this

conclusion of Berzelius was not in accordance with the experimental results. How and by whom, the above statement was corrected ?

6. State and explain—Avogadro's hypothesis. Why is the hypothesis called a law ? What are the important deductions made from it ? Discuss two of the deductions in detail.

7. An element produces several gaseous and volatile compounds. What should be the usual procedure of determining its approximate atomic weight ? What definition of atomic weight does the procedure provide us ?

8. Write notes on : (a) Avogadro's hypothesis and Avogadro's number (b) Atom and molecule (c) Gram-molecule and gram-atom (d) Molecular weight and molar volume

9. Prove : (a) Molecules of hydrogen and oxygen are diatomic (b) One gm-molecule of any gas contains the same number of molecules, (c) The molecular weight of a gas is twice its vapour density, (d) Density and vapour density have different meanings, (e) Avogadro's hypothesis explains Gay Lussac's law of gaseous volumes, (f) Avogadro's hypothesis modifies Dalton's atomic theory

10. Determine the molecular formulae of the gases from the given observations : (a) Chemical combination of 2 volumes of hydrogen and 1 volume of oxygen produces 2 volumes of steam. Vapour density of steam is 9.0, (b) Sulphur dioxide contains its own volume of oxygen, the vapour density of sulphur dioxide being 32.0, (c) Carbon monoxide contains half its volume of oxygen it being given that the relative density of carbon monoxide is 14, (d) Two volumes of nitric oxide contain one volume of oxygen. The vapour density of nitric oxide is 15.

11. Explain the difference between the weight of a molecule of oxygen and molecular weight of oxygen. What do you understand by (a) gram molecular weight and (b) gram molecular volume of oxygen. Give the values of gram-molecular weights and gram molecular volumes of (a) Carbon dioxide, (b) Chlorine, (c) Hydrogen

II

1. (a) Calculate the molecular weight of a gas one litre of which at N.T.P. weighs 1.7 gms. [Ans. 71]

(b) 32 gms of sulphur dioxide gas at N.T.P. occupy a volume of 1120 c.c. What is the molecular weight of the gas ? [Ans. 64]

(c) The volume of 1 gm. of a gas at N.T.P. is 500 c.c. What is the molecular weight of the gas ? [Ans. 44.8]

2. The molecular weight of a gas is 44. Find out the density (gm./litre) of the gas. [Ans. 1.98 gm./litre]

3. Calculate the weight of 20 litres of carbon dioxide at 0°C and 76 cm. Hg.

4. What is the volume of 1 gm. of hydrogen at N. T. P. and how many molecules of hydrogen are present in 1 litre of the gas in this condition ? [Ans. 11.2 litres ; 2.68×10^{23}]

5. 0.1022 gm. of a substance, when vaporised, occupies 49.84 c.c. at S. T. P. Find the gm-molecular weight of the substance. [Ans. 45.92 gms.]

6. 11 gms. of an oxide of nitrogen gave 5.6 litres of nitrogen. 15 gms. of another oxide of nitrogen gave the same volume of nitrogen. (Volume was measured at S. T. P.) Show that these results are in accordance with the law of multiple proportions.

7 Calculate the weight of 20 litres of carbon monoxide at 0°C and 722 mm. pressure.

✓8. 0.034 gm. of a gas occupies 30 c.c. at 27°C and 760 mm. pressure. Find out the molecular weight of the gas. [Ans. 27.89]

✓9. One litre of a gas weighs 1.215 gms. at 27°C and 780 mm. pressure. Calculate the molecular weight of the gas [Ans. 29.13]

✓10. How many gram-molecules of a gas are present in 0.476 litre of the gas at 120°C and 81.3 cm pressure ? Calculate also the number of molecules the gas contains under these conditions. [Ans. 0.017, 1.02×10^{22}].

[N. B. In solving the problems 7, 8, 9, 10, the students will be required to apply the equation of state discussed in chapter 8 of this book.]

11 Calculate the number of molecules of oxygen in 1 c.c. of the gas at N. T. P. What are the molecular weight and actual weight of one molecule of oxygen ?

12 (a) Which mole is heavier and why—one mole of sodium or one mole of oxygen gas ? [Ans. One mole of oxygen gas]

(b) How many atoms are there in 0.635 gm of copper ? [Ans. 6.023×10^{23}]

(c) How many gm-atoms of hydrogen are present in 8.5 gms. of ammonia ?

(d) How many atoms of oxygen are present in 0.90 gm. of water ? [Ans. 3.0115×10^{23}]

(e) How many molecules of water are present in a drop of water weighing 0.05 gram ? [W. B. H. S. (Voc) 1978]

(f) What mass of copper contains ten times as many atoms as 4g of carbon ?

(h) A mixture of hydrogen and oxygen contains 20% by weight of hydrogen. What is the total number of molecules present per gram of the mixture ? [W. B. H. S. 1982 Ans. 6602×10^{23}]

(i) Prove that one gram of nitrogen and one gram of carbon monoxide will contain very nearly the same number of molecules. [W. B. H. S. 1979]

13. (a) Which of the following has the largest number of atoms :

(i) 0.50 gm-atom of copper, (ii) 1.0×10^{23} atoms of copper
(iii) 0.635 gm. of copper. [Ans. 0.50 gm atom of copper]

(b) Which of the following has the smallest number of molecules :

(i) 11.2 litres of SO_2 gas at N. T. P. (ii) 1 gm-molecule of SO_2 gas, (iii) 1×10^{23} molecules of SO_2 gas. [Ans. 1×10^{23} molecules]

(c) Prove that 1 gm. of hydrogen contains greater number of molecules than 1 gm. of carbon dioxide.

14. The volume occupied by a molecule of water has been calculated to be 2.93×10^{-23} ml. The atom of oxygen in this molecule occupies about half of the above volume. What is the approximate diameter of an oxygen atom ? [Ans. 3.056×10^{-8} cm.]

15. A compound on analysis gave 0.062 per cent phosphorus. If each molecule is assumed to contain one atom of phosphorus, what is the molecular weight of the compound ? [Ans. 50,000]

16. One atom of an element 'X' weighs 6.644×10^{-23} gm. Calculate the number of gm-atoms in 40 kg. of it. [Ans. 1000]

17. Complete the following table :

Element	Mass/gm.	Number of moles	Number of particles
Sodium	9.2		
Iron			2×10^{21}
Silver		5	
Copper	2.54		
Carbon		6×10^{-2}	
Hydrogen (H_2)	0.2		
Sulphuric acid			6.02×10^{23}
Water	0.4		

CHAPTER 4 : Symbol, Formula Valency and Equation.

I

1. Symbol, formula and chemical equation have both qualitative and quantitative significance. Justify the statement with suitable examples.

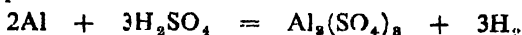
2. Define and illustrate : (a) Symbol, (b) Formula, (c) Valency, (d) Radical, (e) Chemical equation, (f) Empirical formula and molecular formula.

What is the difference between molecular weight and formula weight ?

3. What is valency ? Mention one metal and one nonmetal having more than one kind of valency. Give also the formulae of their oxides and chlorides.

4. (a) What is meant by the term valency ? The valency of hydrogen is taken as the standard in determining the valency of other elements—why ?

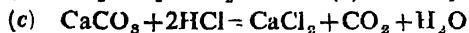
Is it possible to determine the valency of aluminium from the following equation ?



(c) The formula of phosphoric acid is H_3PO_4 . If the formula of the chloride of a metal (M) be MCl_2 , what is the formula of the phosphate of this metal ?

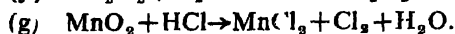
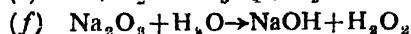
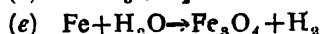
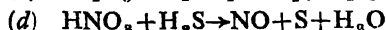
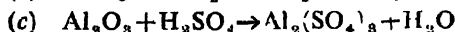
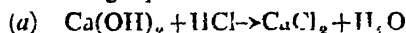
5. What is meant by a chemical equation ? State its significance and limitations.

6. What information regarding the chemical reactions can you get from the following chemical equations ?



Comment on : A chemical equation does not give all information needed for a chemical reaction.

7. Why is it necessary to balance a chemical equation ? Balance the following equations :



8. Give the correct equations of the following reactions.

(a) Phosphorus on being heated with oxygen produces phosphorus pentoxide, (b) Aluminium oxide reacts with sulphuric acid producing aluminium sulphate and water, (c) Under suitable conditions, sulphur di-oxide combines with oxygen to form sulphur trioxide, (d) Magnesium when burnt in nitrogen gives magnesium nitride which reacts with water giving magnesium hydroxide and ammonia, (e) Iron and sulphur on being heated produces ferrous sulphide, (f) Calcium decomposes water giving calcium hydroxide and hydrogen, (g) Ammonia and hydrogen chloride interact to form ammonium chloride, (h) When iron powder is added to a solution of copper sulphate, copper is precipitated and ferrous

sulphate is formed in solution. (i) When stannous chloride solution is added to a solution of ferric chloride, ferrous chloride and stannic chloride are formed. (j) Potassium chlorate on heating gives potassium chloride and oxygen.

9. What are understood by 'empirical formula' and 'molecular formula'? What is the relation between them? In which case, do both the formulae become identical? Explain with suitable examples.

10 (a) "The relative density of sulphur dioxide is 32"—What does the statement mean? What will be the relative density of sulphur dioxide when that of oxygen is taken as unity?

(b) Calculate to show that carbon dioxide is heavier than air.

(c) How many times is carbon dioxide heavier than equal volume of ammonia measured at the same temperature and pressure? Why is the identity of temperature and pressure essential in the above case?

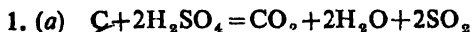
11. Indicate whether the following statements are true or false. Justify your answer.

(a) Empirical and molecular formulae are never the same.

(b) 27 gms. of aluminium react completely with 24 gms. of oxygen.

(c) Mg represents the name of the element magnesium only.

II



With the help of the above equation, calculate the amount of carbon dioxide in grams formed from 19 gms. of sulphuric acid.

(b) 10 gms. of sulphur when burnt in 10 gms. of oxygen yield 20 gms. of sulphur dioxide. Can we get 20 gms. of carbon dioxide by burning 10 gms. of carbon in 10 gms. of oxygen?

(c) 1.60 g. of the oxide of a metal gave 1.28 g. of the metal M ($M=64$) when reduced in hydrogen. Deduce from the data the formula of the oxide and write the equation for the reduction ($O=16$).

(d) When 1.95 g. of metal M ($M=65$) reacted with excess of hot copper sulphate solution, the mass of copper deposited (when purified and dried) was 1.92 g. ($Cu=64$). Show that these figures correspond to the equation. $CuSO_4 + M \rightarrow Cu + MSO_4$.

2. Find the minimum weight of iron required to produce 50 gms. of hydrogen. [Ans. 10.0 gms.]

3. Calculate the weight of iron which will be converted into oxide by the action of 18 gms. of steam. [Ans. 42 gms.]

4. Find the weight of calcium nitrate formed by treating 60 gms. of calcium oxide with 100 gms. of nitric acid. [Ans. 130.16 gms.]

5. What weight of hydrogen will be produced by decomposing 18 gms. of water either by (a) metallic sodium or (b) electrolysis.

[Ans. 1 gm. ; 2 gms.]

6. What changes in weight will be observed on heating sufficiently one gram of each of (i) Hg (ii) $MgCO_3$, (iii) $NaHCO_3$, (iv) KNO_3 .

7. What amount of silver chloride is formed by the action of 5.846 gms. of sodium chloride with excess of silver nitrate solution ?

(Cl=35.46) [Ans. 14.346 gms.]

8. How much manganese dioxide will be needed for complete extraction of bromine from 47.6 gms of potassium bromide ?

(Mn=55, Br=80).

[Ans. 17.4 gms.]

9. Calculate the weight of nitric acid which will be required to produce 16.6 gms. of lead nitrate from 13.4 gms. of lead carbonate.

[Ans. 15 gms.]

10. How much potassium chlorate must be strongly heated to yield as much oxygen as would be obtained from 200 gms. of mercuric oxide ? (K=39, Hg=200)

[Ans. 37.808]

11. Find out the relative weights of potassium chlorate and barium peroxide which will liberate equal amounts of oxygen. (K=39, Ba=137.36)

[Ans. 1 : 4.139]

12. 15.25 gms. of a mixture of potassium chlorate and manganese dioxide were heated and 4.8 gms. of oxygen were liberated. What weight of manganese dioxide was used as catalyst ?

[Ans. 3 gms.]

13. 24.5 gms. of potassium chlorate are heated to produce oxygen. Hydrogen is generated by the action of dilute sulphuric acid on zinc. What weight of zinc will be required to produce just sufficient hydrogen to combine completely with oxygen obtained from the potassium chlorate ?

[Ans. 39.0 gms.]

14. 7.0 gms. of magnesium carbonate were added to double its weight of dilute sulphuric acid. After the reaction had ceased, it was found that 0.7 gm. remained undissolved. Calculate the percentage strength of the acid.

[Ans. 52.5%]

15. What weight of $CaCO_3$ must be decomposed with HCl to yield sufficient CO_2 to convert 100 gms. of sodium hydroxide to sodium carbonate ?

[Ans. 125 gms]

16. How much copper will be obtained when cupric oxide is completely reduced by hydrogen produced by the action of excess of zinc on 10 gms. of sulphuric acid ?

[Ans. 6.48]

17. 10 c.c. of a solution of hydrochloric acid when treated with an excess of silver nitrate solution give 0.1435 gm. of silver chloride. Find how many grams of HCl are present in one litre of this solution ?

[Ans. 3.65 gms.]

18. 20 c.c. of a sample of hydrochloric acid (sp. gr. 1.55) were added to 15 gms. of marble. After the reaction was complete, the undissolved marble was filtered off, washed, dried and was found to

weigh 5.5 gms. Calculate the percentage weight of hydrochloric acid in the sample. [Ans. 22.35%]

19. Calculate the number of molecules present in hydrogen liberated by the action of 1 gm. of magnesium on excess of dilute sulphuric acid.

20. 1.5 gms. of a sample of marble containing some silica as impurity were mixed with 3 gms. of sulphuric acid. When all action had ceased, 1.575 gms. of the acid were found to remain unreacted. Calculate the percentage of CaCO_3 in the marble. [Ans. 96.98%]

21. A mixture contains CaCO_3 and CaO . 20 gms. of the mixture, when heated, gave 6.6 gms. of carbon dioxide. What is the percentage of CaCO_3 in the mixture? [Ans. 75%]

22. 1.0 gm. of a sample of aluminium containing some silica as impurity gave 0.05 gm. of hydrogen when treated with hydrochloric acid. What is the percentage of aluminium in the mixture? [Ans. 45%]

23. 12 gms. of a mixture of potassium chlorate and chloride gave on heating 3.8 gms. of oxygen. Find the percentage of potassium chlorate in the mixture. ($K=39.1$, $Cl=35.5$) [Ans. 80.8%]

24. 3.60 gms. of a mixture of sodium and potassium chlorides gave with silver nitrate 7.4 gms. of silver chloride. What is the percentage of each salt in the mixture?

[Ans. $\text{NaCl} = 42.59\%$; $\text{KCl} = 57.41\%$]

25. 5 gms. of a dry mixture of sodium carbonate and sodium bicarbonate, on heating lose 0.55 gm. in weight. Find how much Na_2CO_3 was present in the mixture. [Ans. 2.9 gms.]

26. 0.6 gm. of a sample of sodium chloride when treated with silver nitrate solution gave 1.37 gms. of silver chloride. Calculate the percentage of purity of the sample of sodium chloride.

[Ans. 93.1%]

27. A mixture of cuprous and cupric oxide was found to contain 88% copper. Calculate the proportion of the two compounds in the mixture. [Ans. $\text{Cu}_2\text{O} = 90\%$, $\text{CuO} = 10\%$]

28. 2.5 gms. of a mixture of copper and cupric oxide on being reduced in a current of hydrogen, gave 2.098 gms. of copper. What was the percentage of copper in the mixture? [Ans. $\text{Cu} = 20\%$]

29. Sea water containing 2.64% by weight of common salt has a specific gravity of 1.03. Find the amount of sulphuric acid that would be required to completely convert the sodium chloride obtained from one litre of sea water into sodium sulphate.

[Ans. 2.277 gms.]

30. Calculate the weight of MnO_2 and the volume of hydrochloric acid of specific gravity 1.12 containing 40 percent HCl by weight, needed to prepare 1.78 litres of chlorine at S.T.P. ($\text{Mn} = 54.9$; $\text{Cl} = 35.5$) [Ans. 6.905 gm. MnO_2 ; 25.91 ml. HCl]

31. 1.48 gms of a mixture of calcium carbonate and magnesium carbonate gave on ignition 0.96 gm. of constant weight residue. What is the percentage composition of the mixture ?

[Ans. $\text{CaCO}_3 = 54.35\%$; $\text{MgCO}_3 = 45.65\%$]

32. 0.9031 gm of a mixture of sodium chloride and potassium chloride on treatment with sulphuric acid yields 1.0784 gms. of a mixture of sodium sulphate and potassium sulphate. Calculate the percentage of sodium chloride and potassium chloride in the mixture.

[Ans. $\text{NaCl} = 58.1\%$; $\text{KCl} = 41.9\%$]

33. Equal weights of mercury and iodine are allowed to react completely to form a mixture of mercurous and mercuric iodides. Calculate the ratio of the weights of mercurous and mercuric iodides formed.

[Ans. Mercurous : Mercuric = 1.936:1]

✓ 34. Calculate the weight of potassium chlorate which on heating will liberate 2.73 litres of oxygen at N.T.P. [Ans. 9.9531 gm.]

✓ 35. How many grams of ammonium chloride would be required to prepare 10 litres of ammonia at 0°C and 760 mm. pressure ?

✓ 36. Calculate the weight and volume of oxygen produced by electrolysis of 18 gms. of water. [Ans. 16 gms, 11.2 litres]

37. What volume of sulphur dioxide would you get at 0°C and 760 mm pressure by burning hydrogen sulphide obtained from 11 gms of ferrous sulphide ? [Ans. 2.8 litres]

38. Calculate the volume of a solution of sulphuric acid of density 1.8 and containing 89% of the pure acid, that would be required to make 2000 c.c. of sulphur dioxide at N.T.P. by acting on sodium sulphite. [Ans. 5.462 c.c.]

39. 100 c.c. of methane at 27°C and 750 mm. pressure were exploded with an excess of oxygen. Determine the weight of water and the volume of carbon dioxide formed at N.T.P.

[Ans. wt. of $\text{H}_2\text{O} = 0.1443$ gm ; vol of $\text{CO}_2 = 89$ cc]

40. What volume of nitric acid (sp. gr. 1.46) containing 60% of the acid by weight will react with 10 gms. of cupric oxide ? ($\text{Cu} = 63.5$) [Ans. 18.09 cc]

41. A sample of marble contains some silica as impurity. 2.0 gms. of the sample on being heated give 433.6 c.c. of carbon dioxide at N.T.P. Calculate the percentage of CaCO_3 in the marble. [Ans. 96.8%]

42. 1 gm of iron is converted into ferric chloride and the product is dissolved in water. What volume of H_2S at N. T. P. will be theoretically required to reduce completely the ferric chloride to ferrous chloride ?

43. 1 litre of oxygen at N.T.P, is allowed to react with 2 litres of carbon monoxide under the identical conditions. Calculate the weight of carbon dioxide formed. [Ans. 3.93 gms.]

44. A current of hydrogen is passed over cupric oxide heated

in a bulb. Calculate the volume of hydrogen at N.T.P. required for the reduction of 0.8 gm. of the oxide. [Ans. 0.252 litre]

45. Determine the volume of carbon dioxide formed at N.T.P. by burning acetylene produced from 48 gms. of calcium carbide [Ans. 33.6 litres]

46. 1 gm. of a mixture of sodium carbonate and bicarbonate in equal proportions by weight is ignited until there is no more loss in weight. What volume of carbon dioxide is evolved at N.T.P. ? [Ans. 66.67 c.c.]

47. What weight of potassium chlorate, on being heated, will yield oxygen just sufficient for the complete combustion of 1520 c.c. of a mixture of 20% CH_4 and 80% CO at 27°C and 760 mm. ?

48. A balloon of 1000 litres capacity is to be filled with hydrogen at 27°C and 750 mm. pressure. Calculate the minimum quantity of iron required to liberate the necessary amount of hydrogen. ($\text{Fe}=56$). [Ans. 2245.05 gms.]

49. Calculate the weights of manganese di-oxide needed to prepare 10 litres of chlorine at N.T.P. and at 27°C and 750 mm. pressure by its reaction with excess of hydrochloric acid. [Ans. 388.34 gms ; 347.56 gms]

50. Air contains 23 per cent of its weight of oxygen. How many grams of sulphur will be required to burn out the oxygen in 100 litres of air at 30°C and 755 mm. ? (density of air (14.4) [Ans. 26.68 gms.]

51. A sample of potassium chlorate contains a little potassium chloride as impurity. Oxygen obtained by heating 13 gms of the sample is found to react completely with 7.484 litres of hydrogen at 27°C and 750 mm. pressure. Calculate the amount of potassium chloride present in the mixture. [Ans. 0.75 gm]

52. Find out the amount of iron and zinc in the mixture if 2.33 gms. of the mixture gave 896 ml of hydrogen (at N.T.P.) when dissolved in an acid. [Ans. $\text{Fe}=1.7$ gms., $\text{Zn}=0.63$ gms.]

53. How much pure calcium carbonate is required to give 500 c. c. of CO_2 at 27°C and 760 mm. pressure ? How much of pure carbon will be needed to produce the same amount of carbon dioxide ? [Ans. $\text{CaCO}_3=2.03$ gms., $\text{C}=0.244$ gms.]

54. What weight of silver chloride is precipitated when 105 c.c. of hydrogen chloride measured at 15°C and 770 mm pressure are absorbed by silver nitrate solution ? ($\text{H}=1$, $\text{Ag}=108$, $\text{Cl}=35.5$) [Ans. 0.646 gm]

55. (a) What volume of carbon monoxide can be obtained theoretically from 100 litres of carbon dioxide both measured under standard conditions of temp. and pressure ? [Ans. 200 litres]

(b) What volume of carbon dioxide will be obtained when 100 litres of carbon monoxide and requisite quantity of oxygen interact at N.T.P. ? [Ans. 100 litres]

56. Find the volume of nitrogen which can be liberated from ammonia by 90 c. of chlorine at N.T.P.

57. What volume of air containing 20% oxygen by volume would be required for complete combustion of 5 litres of acetylene and what would be the volume of carbon dioxide produced? (all volumes are measured under the same conditions of temp. and pressure).

58. When a silent electric discharge is passed through 25 c.c. of oxygen, the volume reduces to 20 c.c. Find out the composition of the resulting gas mixture. [Ans. $O_3 = 10$ c.c., $O_2 = 10$ c.c.]

59. 25 c.c. of a mixture of gases containing nitrogen and nitric oxide are passed over ignited metallic copper and the resultant gas collected and is found to occupy 20 c.c. Ascertain the percentage composition of the original mixture, gases being measured at the same temperature and pressure. [Ans. $N_2 = 60\%$, $NO = 40\%$]

60. What volume of oxygen will be needed to convert 1 litre of nitric oxide into nitrogen peroxide under the same conditions of temperature and pressure. Calculate the volume of N_2O_4 formed.

61. Half a litre of carbon dioxide is passed over red hot carbon. The volume becomes 700 c.c. Find the composition of the product, assuming that all the gases are measured at N.T.P.

[Ans. $CO_2 = 300$ c.c., $CO = 400$ c.c.]

62. A gas-mixture contains 46% hydrogen, 40% methane and 14% ethylene. What volume of air will be needed to oxidise 100 litres of the gas mixture? Air is found to contain 21% of oxygen by volume.

63. 20 c.c. of ethylene at N.T.P. are exploded with 100 c.c. of oxygen at N.T.P. and than the resulting gas mixture is treated with KOH solution. What would be the volume at N.T.P. of the gas mixture obtained at the end of each of the above two steps?

[Ans. 80 c.c. ; 40 c.c.]

64. 80 c.c. of carbon monoxide are mixed with 30 c.c. oxygen and exploded. If the resulting mixture is shaken with a solution of caustic potash, what volume of the gas will remain and what gas will it be?

[Ans. 20 c.c. of CO]

65. 30 c.c. of a mixture of methane and hydrogen were mixed with 60 c.c. of oxygen and exploded. On cooling, the volume was found to be 52.5 c.c. On introducing KOH, the volume was reduced to 37.50 c.c. Find the weight of each of the gases in the mixture. (All volumes were measured at the same temperature and pressure).

[Ans. $CH_4 = 0.0108$ gm., $H_2 = 0.00135$ gm.]

66. 10 c.c. of a mixture of methane, carbon monoxide and nitrogen exploded with excess of oxygen gave a contraction of 6.5 c.c. There was a further contraction of 7 c.c. when the residual gas was treated with caustic potash. What was the composition of the original mixture? [Ans. $CH_4 = 2$ c.c. ; $CO = 5$ c.c. ; $N_2 = 3$ c.c.]

67. 10 c.c. of a mixture of methane, ethylene and carbon dioxide were exploded with excess of air. After explosion, there was a contraction of 17 c.c. and after treatment with KOH, there was a further reduction of 14 c.c. What was the composition of the mixture. [Ans. $\text{CH}_4 = 4.5$ c.c. ; $\text{C}_2\text{H}_4 = 4$ c.c. ; $\text{CO}_2 = 1.5$ c.c.]

68. 100 c.c. of a mixture of carbon monoxide, methane and hydrogen were mixed with 300 c.c. of oxygen and fired. After cooling, the resulting gases occupied 285 c.c. and after absorption by potash 205 c.c. of oxygen remained. Determine the composition of the mixture. All the gases measured at the same temperature and pressure. [Ans. $\text{CO} = 50$ c.c. ; $\text{CH}_4 = 30$ c.c. ; $\text{H}_2 = 20$ c.c.]

69. 100 c.c. of water gas containing some carbon dioxide were exploded with 100 c.c. of oxygen and the volume after explosion was 100 c.c. On introducing NaOH, the volume was reduced to 52.5 c.c. Find the percentage composition of the mixture.

[Ans. $\text{CO} = 42.5$ c.c. ; $\text{H}_2 = 52.5$ c.c. ; $\text{CO}_2 = 5$ c.c.]

70. 20 c.c. of ammonia gas was enclosed in a eudiometer tube and exploded. The volume after explosion was 40 c.c. To this 45 c.c. of oxygen was added and the mixture again exploded. On cooling, the volume of the residual gases was found to be 40 c.c. Calculate the formula of ammonia from the above combustion data.

71. 10 c.c. of nitrous oxide were taken in a eudiometer tube and mixed with hydrogen. The volume after addition of hydrogen was 28 c.c. The mixture when exploded occupied 18 c.c. Then, by adding oxygen, the volume was raised to 27 c.c. and the mixture was again exploded. The volume after the second explosion was found to be 15 c.c. Find the formula of nitrous oxide from the data given. All volumes are taken at N.T.P. [Ans. N_2O]

72. 20 c.c. of a gaseous hydrocarbon were exploded with 66 c.c. of oxygen. The residual gases after cooling occupied 56 c.c. On treatment with KOH, the volume decreased to 16 c.c. What is the formula of the hydrocarbon ? [Ans. C_3H_8]

73. 10 c.c. of a gaseous hydrocarbon are exploded with 250 c.c. of carbon dioxide-free oxygen. A contraction of 40 c.c. was observed. On absorbing in KOH, the volume of CO_2 is found to be 40 c.c. What is the molecular formula of the hydrocarbon ?

74. 12 c.c. of a gaseous hydrocarbon were mixed with 90 c.c. of oxygen and the mixture was exploded in a eudiometer ; after explosion, the volume of the mixture was 72 c.c. and on adding KOH, 36 c.c. of it disappeared leaving only oxygen. What was the gas ?

75. 50 vols of a gas mixed with 70 vols of oxygen give after explosion 50 vols of carbon dioxide and after absorption by KOH, explosion 50 vols of carbon dioxide and after absorption by KOH, 45 vols of oxygen are left. What is the gas ? [Ans. CO]

76. 15 c.c. of a gaseous hydrocarbon for its complete combustion require 357 c.c. of air containing 21% oxygen by volume. The volume of resulting gas mixture is 327 c.c. (all volumes are

measured at the same conditions of temperature and pressure) Determine the molecular formula of the hydrocarbon. Neglect the volume of water formed. [Ans. C_8H_8]

77. 12 c.c. of a gaseous hydrocarbon when exploded with excess of oxygen underwent a contraction of 24 c.c. and on being treated with KOH, a further contraction of 12 c.c. occurred. What is the formula of hydrocarbon ? [Ans. CH_4]

78. 12 c.c. of gaseous hydrocarbon is exploded with excess of oxygen. The contraction observed is 30 c.c. When the residual gas is treated with KOH, there is a contraction of 24 c.c. What is the formula of the hydrocarbon ? [Ans. C_2H_6]

79. 12 c.c. of a gaseous hydrocarbon were mixed with 90 c.c. of oxygen and exploded. After explosion, the volume was 72 c.c. and after treatment with KOH, it was 36 c.c. (Found to be oxygen). What is the molecular formula of the hydrocarbon ? [Ans. C_2H_4]

80. A gaseous hydrocarbon on combustion gives its own volume of carbon di-oxide. What is the molecular formula of the hydrocarbon if its density be 14 ?

81. 20 c.c. of a gaseous hydrocarbon are exploded with oxygen avoiding excess. On cooling, the volume contracts by 60 c.c. The density of the hydrocarbon is 22. Find out the formula of the hydrocarbon. [Ans. C_3H_8]

82. 10 c.c. of a gaseous hydrocarbon are exploded with 25 c.c. of oxygen. The mixture contracts to 15 c.c. On adding KOH, a further contraction of 10 c.c. takes place and the residue is pure oxygen. What is the formula of the hydrocarbon if its density be 8 ? [Ans. CH_4]

83. (a) The molecular formula of an organic compound is $C_8H_8O.NBrS$. Find its percentage composition.

(b) 1.279 gms. of an organic compound containing carbon, hydrogen, oxygen and nitrogen gave 1.50 gms. of carbon di-oxide and 0.77 gm. of water on combustion.

Analytical result shows that 0.8125 gm. of the compound contains 0.108 gm. of nitrogen. What is the empirical formula of the compound ? [Ans. $C_8H_7O_8N$]

(c) A molecule of sulphur dioxide contains one atom of sulphur and two atoms of oxygen. The compound contains 50% sulphur by weight. What is the ratio of the atomic weights of sulphur and oxygen.

(W.B.H.S. 1979)—[Ans. At. wt. of S : At. wt. of oxygen = 2 : 1]

84. An organic compound contains carbon, hydrogen, oxygen and nitrogen. 0.145 gm. of this gas on complete combustion 0.198 gm. of CO_2 and 0.108 gm. of water. The same weight of the compound on analysis yielded 16.8 c.c. of nitrogen at N.T.P. Deduce the empirical formula of the compound. [Ans. $C_7H_8NO_2$]

85. A gaseous compound of carbon and nitrogen containing 53.8 per cent by weight of nitrogen was found to have a vapour density of 25.8. What is the molecular formula of the compound ?

[Ans. C_2N_2]

86. A compound of carbon, hydrogen and oxygen contains 40% carbon, 6.66% hydrogen and the rest is oxygen. Molecular weight of the compound is 60. Find the empirical and molecular formula of the compound.

[Ans. CH_3O ; $C_2H_4O_2$]

87. A compound of carbon, hydrogen and nitrogen contains three elements in the respective ratio of 9 : 1 : 3.5 grams. Calculate its empirical formula if its molecular weight be 108. What is the molecular formula ?

[Ans. C_8H_4N ; $C_8H_8N_2$]

88. Analytical result of an organic compound is stated below :

Carbon \rightarrow 40.65% ; hydrogen \rightarrow 8.55% and nitrogen 23.7%

Vapour density of the compound is 29.5. Find out the empirical formula and molecular formula of the compound-

[Ans. both C_2H_5NO]

89. The empirical formula of a compound is CH_2O and its vapour density is 45. What is the molecular formula of the compound ?

90. A gaseous hydrocarbon contains 85.62% carbon and 14.38% hydrogen. Density of the hydrocarbon is 1.26 gms./litre. Determine its molecular formula.

91. A compound gave on analysis the following results :

H = 1.59%, O = 76.09% and N = 22.32%, 333.4 ml. of the vapour of the compound weigh 0.939 gm. at N.T.P. Determine the molecular formula of the compound.

[Ans. HNO_3]

92. An element E forms two gaseous hydrides A and B which contain 75 and 80 per cent of E and have densities of 8 and 15 respectively. Given that A contains only one atom of E in its molecule, calculate the atomic weight of E and the formulae of A and B.

[Ans. 12, $A \rightarrow EH_4$, $B \rightarrow E_2H_6$]

93. 367 gms. of an organic compound containing carbon, hydrogen and oxygen only, yielded on complete combustion 3.002 gms. of carbon di-oxide and 1.640 gms. of water. What is the empirical formula of the compound ?

[Ans. $C_8H_8O_2$]

94. 0.2012 gm. of an organic compound containing carbon, hydrogen and oxygen when heated strongly with excess of cupric oxide gave 0.4431 gm. of carbon di-oxide and 0.1462 gm. of water. The molecular weight of the compound was found to be 100. What is its molecular formula ?

[Ans. $C_6H_8O_2$]

95. A compound contains 10.05% carbon, 0.84% hydrogen and 89.1% chlorine. Its density in the gaseous state at $150^\circ C$ and 760 m.m. pressure is 3.43 gms./litre. What are its empirical formula and molecular formulae ?

96. Carbohydrates are compounds containing only carbon, hydrogen and oxygen having the atomic ratio of H:O as 2:1. When heated in the absence of air, these compounds decompose to form carbon and water:

(a) If 310 gms. of a carbohydrate leave a residue of 124 gm. of carbon on heating in absence of air, what is the empirical formula of the carbohydrate? [Ans. $C(H_2O)$]

(b) If 0.633 mole of the carbohydrate contains 1.00 gm. hydrogen. What is the molecular formula of the carbohydrate?

[Ans. $C_6H_{12}O_6$]

97. 0.9 gm. of a solid organic compound (molecular weight 90) containing carbon, hydrogen and oxygen, was heated with oxygen corresponding to a volume of 224 ml at S.T.P. After combustion, the total volume of the gases was 160 ml at S.T.P. On treatment with potassium hydroxide, the volume decreased to 112 ml. Determine the molecular formula of the compound [Ans. $C_6H_8O_4$]

98. Carbon combines with hydrogen to form three compounds A, B and C. The percentages of hydrogen in A, B and C are 25, 14.3 and 7.7 respectively.

(i) Find the empirical formulae of the compounds. (ii) What law of chemical combination does this example illustrate?

[Ans. (i) CH_4 , CH_3 , CH ; law of multiple proportions]

CHAPTER 5 Equivalent Weight

I

1. What are meant by equivalent weight and gram-equivalent of an element? "Equivalent weight of an element may vary"—Discuss. Describe one method for the determination of the equivalent weight of copper. How would you calculate the equivalent weight from the experimental data?

2. Give a brief account of the different methods applied for the determination of the equivalent weight of elements. Describe in detail any of the two methods you have mentioned.

3. How is the equivalent weight of an element related to its atomic weight? State the condition under which they have the same value? Give two illustrations. Which of the following of an element must be a whole number?

(i) Equivalent weight (ii) Valency (iii) Atomic weight.

4. (a) "The equivalent weight of an element depends on the reaction it undergoes."—Explain the statement with reference to the following pair of reactions.



(b) Why does the equivalent weight of some elements not remain the same in all their reactions ?

5. Describe the experimental procedures for the determination of equivalent weight of oxygen and carbon.

6. How is the equivalent weight of zinc determined by the displacement of hydrogen from an acid ? How is the equivalent weight calculated from the experiment data ? State why this method is not applicable in determining the equivalent weights of sodium and copper.

7. Explain why in the determination of equivalent weight of zinc.

(a) the weight of zinc taken should be between 0.08 gm. and 0.10 gm.

(b) the procedure is not carried out in a Woulfe's bottle.

(c) an inverted funnel is used to cover the watch-glass containing the piece of zinc.

(d) excess of sulphuric acid is used for its reaction with zinc.

(e) a few drops of CuSO_4 solution are required to be added before the start of hydrogen displacement.

(f) addition of sufficient quantity of CuSO_4 is not justifiable

(g) the volume of hydrogen collected in the eudiometer is read only after shifting the eudiometer to a tall jar containing water.

(h) barometer and thermometer readings are taken at the time of noting the volume of hydrogen displaced.

(i) aqueous tension corresponding to the thermometer-reading has to be noted.

8. (a) Describe a method based on the addition of oxygen for determining the equivalent weight of an element.

(b) Describe a method based on removal of oxygen for determining the equivalent weight of an element.

9. Discuss in brief the methods of determination of the equivalent weight of sodium and silver.

10. Describe briefly the method of determining the equivalent weight of copper starting from pure metallic copper.

11. What do you mean by the terms (a) atomic weight and (b) gram-atomic weight ? Explain the statement "The atomic weight of nitrogen is 14.00". How is the exact atomic weight of an element determined ?

12. Given the atomic weight of chlorine, how can the atomic weight of silver be determined experimentally.

13. State Dulong and Petit's law and show how with the help of this law the atomic weight of an element can be determined. State the limitations of this process.

14. What are isomorphous substances ? State Mitscherlich's law of isomorphism. How would you determine the atomic weight of an element by this law ?

Describe the tests that may be employed to ascertain if two salts are isomorphous

15. (a) Explain what is meant by (i) the equivalent weight of aluminium is 8.99 (ii) atomic weight of aluminium is 26.97.

Name the element whose equivalent weight is 12. What are the other informations necessary to determine its atomic weight ?

(b) The atomic weight of an element is 24. One atom of the element combines with two atoms of chlorine. What is the equivalent weight of the element ?

16. The equivalent weights of zinc, copper and silver are determined by the hydrogen displacement, oxide formation and chloride formation methods respectively. Explain why different methods are applied in cases of these three metals.

17. Indicate whether the following statements are true or false. Justify your answer.

(i) Equivalent weight of an element is always the same.

(ii) Valency of an element must always be denoted by a whole number.

(iii) The method of hydrogen displacement from an acid cannot be applied in the case of determination of equivalent weight of copper

iv) Two substances having the same crystalline form are isomorphous

II

✓ 1. The oxide of a metal contains 71.4% of the metal. What is the equivalent weight of the metal. [Ans. 17.97]

✓ 2. 0.108 gm. of a metal when dissolved in dilute sulphuric acid evolves 100 ml. of dry hydrogen at N.T.P. Calculate the equivalent weight of the metal. [Ans. 12.096]

✓ 3. Find out the volume of hydrogen produced at N.T.P. by the action of dil. sulphuric acid on 1.45 gms. of a metal. The equivalent weight of the metal is 9. [Ans. 1.819 litres]

4. Find the equivalent weights of copper and oxygen from the data given. Dry hydrogen is passed over 1.58 gms. of heated cupric oxide. The water formed weighs 0.36 gm. and the copper left after the experiment is 1.26 gms. [Ans. Cu = 31.5 ; O = 8]

✓ 5. Pure and dry hydrogen was passed over excess of strongly heated cupric oxide. The oxide lost 1.5938 gms. in weight and 1.79462 gms. of water were formed. Calculate the equivalent weight of oxygen. [Ans. 8]

6. 0.3975 gm. of copper oxide was heated in a current of pure and dry hydrogen till completely reduced and the gaseous product was passed through a tube containing fused calcium chloride previously weighed. The gain in weight of the latter was 0.09 gm. Calculate the equivalent weight of copper. [Ans. 31.75]

7. 0.6842 gm. of copper was dissolved in nitric acid and the solution was carefully evaporated to dryness. When the solid residue was strongly heated, 0.8567 gm. of cupric oxide was produced. Calculate the equivalent weight of copper.

8. 1.0813 gms. of iron gave 3.1439 gms. of ferric chloride. Calculate the equivalent weight of iron in this compound. Find the valency of iron in ferric chloride (Eq. wt. of chlorine = 35.5; At. wt. of iron = 55.85) [Ans. 3]

9. 1.73 gms. of cupric sulphide contain 1.15 gms. of copper. Hydrogen sulphide contains 94.1% sulphur. Find out the weight of copper. [Ans. 31.87]

10. 0.1827 gm. of the chloride of a metal can be quantitatively converted into 0.1057 gm. of its oxide. Calculate the equivalent weight of the metal. (Cl = 35.5) [Ans. 29.74]

11. The equivalent weight of sodium is 23 and that of chlorine is 35.46. What is the percentage of sodium in sodium chloride?

[Ans. 39.34%]

12. 1.5276 gms. of CdCl_2 contain 0.9376 gm. of cadmium. Calculate the atomic weight of cadmium [Ans. 112.52]

13. The oxide of a solid metallic element contains 65.2% of the element. Its atomic weight is 45. What is the valency of the element? [Ans. 3]

14. If a solid element burns in oxygen without any change in volume (of gas) under the same conditions of temperature and pressure and if the pure gaseous product has a density of 32, what is the equivalent weight of the element? [Ans. 8]

15. What weight of a metal of equivalent weight 12 will liberate 525 c.c. of dry hydrogen at 15°C and 750 mm. pressure?

[At N.T.P. 1 litre of hydrogen weighs 0.09 gm.]

16. 2.87 gms. of silver chloride are obtained from 1.49 gms. of potassium chloride. Calculate the equivalent weight of potassium. [Ans. 39.0]

17. 0.1903 gm. of a metal carbonate on being reacted with dilute sulphuric acid gives 0.2589 gm. of anhydrous metal sulphate. What is the equivalent weight of the metal. [Ans. 20.04]

18. 0.5395 gm. of a metallic element yields 0.7175 gm. of its chloride. The specific heat of the element is 0.059. Calculate the exact atomic weight of the element [Ans. 107.6]

19. (a) The equivalent weight of an element is 18.6, and its specific heat is 0.124. What is the valency of the element? Determine the exact atomic weight of the element.

(b) A sample of a metal oxide weighing 6.500 gms. is decomposed quantitatively to give 6.251 gms. of the metal. The specific heat of the metal is 0.0332 cal/g. Calculate the exact atomic weight of the metal and the empirical formula of the oxide.

[Ans. 200.8 ; M_2O]

20. The relative density of the chloride of an element is 59. The chloride contains 9.23 per cent of the element. Find the atomic weight of the element.

[Ans. 10.815]

21. The oxide of an element contains 53.3% of oxygen. The molecular weight of the chloride of the element is 170. Find the valency and atomic weight of the element.

[Ans. 4 ; 28.04]

22. A metal M forms a volatile chloride containing 80% of chlorine. The vapour density of the chloride is 66.75. Calculate exact atomic weight of the element.

[Ans. 26.625]

23. One gram of the chloride of an element was found to contain 0.835 gm. of chlorine. Its vapour density was 85. Find out its molecular formula.

[Ans. MCl_4 where M = symbol of the element]

24. The equivalent weight of an element is 4. It forms a chloride whose vapour density is 59.25 ; Calculate the atomic weight and valency of the element.

25. The chloride of an element contains 58.65% of chlorine. The vapour density of the chloride is 91 times as heavy as an equal volume of hydrogen at N.T.P. Find the equivalent weight, atomic weight and valency of the element.

[Ans. 25, 75, 3]

26. A metallic chloride contains 54.42% chlorine, (At. wt. of chlorine is 35.5). The vapour density of the chloride is 8.16 (0 = 1). What is the equivalent weight of the metal ? Write down the formula of the chloride

27. 0.125 gm. of the chloride of the metal contains 0.054 gm. of the metal. The specific heat of the metal is 0.281. Calculate its atomic weight. (At. wt. of chlorine is 35.5).

[Ans. 27]

28. The vapour density of a metallic chloride in the vaporous state is 66.8. One gram of the chloride with excess of silver nitrate gave 3.225 gms. of silver chloride. Calculate the atomic weight of the metal.

[Ans. 26.94]

29. 65.4 gms. of a metal liberate 22.4 litres of hydrogen from an acid at N.T.P. What is the equivalent weight of the metal ? The metal forms a volatile chloride whose vapour density is 68.2. Calculate the atomic weight of the metal.

[Ans. 32.7 ; 65.4]

30. 0.51 gm. of silver nitrate is required for complete preprecipitation of chlorine from 0.22 gm. of a metallic chloride. The specific heat of the metal is 0.057. Calculate the atomic weight of the metal.

31. Potassium selenate is isomorphous with potassium sulphate and contains 35.77 per cent of selenium. Calculate the atomic weight of selenium (Se).

[Ans. 79.16]

32. A metal M forms a chloride which is isomorphous with potassium chloride. Potassium chloride contains 47.65% of chlorine. Calculate the atomic weight of M. [Ans. 85.8]

33. (a) A metallic chloride contains 25.87% of chlorine and is isomorphous with KCl. What is the atomic weight of the metal? [Ans. 101.7]

(b) The equivalent weight of an element is 13.16. It forms an acidic oxide which with potassium hydroxide, forms a salt isomorphous with K_2SO_4 . Deduce the atomic weight of the element. [Ans. 78.96]

34. The oxides of two metals A and B are isomorphous. The atomic weight of A is 52 and the vapour density of its chloride is 79. The oxide of the element B contains 87.1% of oxygen. Calculate the atomic weight of B.

35. A compound containing 28.2 potassium, 25.6% chlorine and rest oxygen is isomorphous with another compound containing 4.7% potassium, 34.8%, manganese (Mn) and rest oxygen. What is the atomic weight of manganese, if that of chlorine is 35.46? [Ans. 55.01]

36. Potassium selenate which contains 35.77% of selenium is isomorphous with potassium sulphate. Potassium sulphate contains 18.39% of sulphur. If the atomic weight of sulphur be 32, calculate the atomic weight of selenium. [Ans. 79.2]

37. In two isomorphous compounds Cu_2S and Ag_2S , percentages of sulphur are 20.14 and 12.94 respectively. Atomic weight of copper is 63.57. What is the atomic weight of silver? [Ans. 107.9]

38 (a) The sulphate of a metal contains 20.9% of the metal and is isomorphous with $ZnSO_4 \cdot 7H_2O$. What is the possible atomic weight of the metal? [Ans. 58.66]

(b) A metal M forms a sulphate which is isomorphous with magnesium sulphate, $MgSO_4 \cdot 7H_2O$. Calculate the atomic weight of the metal M when 0.6538 gm. of the metal M displaces 2.16 gm. of silver from silver nitrate solution. [Ans. 65.38]

39. 1.112 gms of aluminium form 2.109 gms of its oxide. The sulphate of the metal forms a double salt with potassium sulphate which is isomorphous with chrome alum $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$. The atomic weight of chromium is 52. What is the atomic weight of aluminium? [Ans. 26.76]

40. 0.4686 gm of a metal oxide yields on reduction 0.3486 gm. of the metal which forms an alkali double sulphate isomorphous with common alum. Find the atomic weight of the metal. [Ans. 23.24]

41. Magnesium sulphate contains 9.75% of Mg and 39.02% of SO_4 and zinc sulphate contains 22.6% of Zn and 35.5% of SO_4 . If the atomic weight of zinc be 65, find the atomic weight of magnesium. The two salts are isomorphous. [Ans. 24.05]

42. Prove from the following results that mercury is monatomic.

(a) 10 gms. of mercury combine with 0.8 gms. of oxygen to form an oxide.

(b) 100 c.c. of vapour of mercury at N.T.P. weigh 8.923 gms.

(c) The specific heat of the metal is 0.033.

Solve the following problems using mole concept.

43. Calculate the number of moles in a litre of water.

[Ans. 55.55]

44. (a) 100.60 gms. of a compound contain :

37.2 gms. of carbon, 7.8 gms. of hydrogen and 55.0 gms. of chlorine. From this data calculate :

(i) the number of moles of each element present in the sample

(ii) the number of atoms of each type present in the sample

(b) How many grams of calcium carbonate be heated to get enough carbon dioxide which can convert 0.1 mole of sodium carbonate into sodium bicarbonate ?

[Ans. 0.1 mole]

45. How many grams of water will be formed by passing electric spark through a mixture of 15 gms. of hydrogen and 150 gms. of oxygen ? How many grams of oxygen will remain unreacted ?

[Ans. water \rightarrow 135 gms ; oxygen \rightarrow 30 gms.]

46. Calculate the volume at N.T.P. of carbon dioxide obtained by heating a mixture of 1 gm-molecule of sodium bicarbonate and 1 gm-molecule of sodium carbonate.

[Ans. 11.2 litres]

47. How many c.c. of sulphur dioxide at N.T.P. will be evolved by the action of 20 gms. of sodium sulphite of 90% purity on 5.462 c.c. of sulphuric acid. The acid supplied contains 89% of the pure acid and its density is 1.8.

[Ans. 2000 c.c. (approx)]

48. What volume of hydrogen measured at N.T.P. would be required to reduce completely 0.8 gm. of cupric oxide ? (Cu = 63.57)

[Ans. 0.224 litre]

49. Find out the relative volumes of oxygen when 10 gms. each of potassium nitrate and potassium chlorate are separately decomposed to produce the gas.

[Ans. 1 : 2.427]

50. On adding silver nitrate solution to a solution containing 1.2 gms. of a mixture sodium chloride and potassium chloride, 2.869 gms. of silver chloride are precipitated. Find the amount of sodium chloride in the mixture.

[Ans. 1.169 gms.]

51. 1 gram of an alloy of aluminium and magnesium reacts with excess of hydrochloric acid to form 1.104 litres of hydrogen at N.T.P. What is the composition of the alloy ?

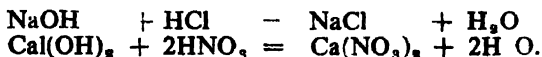
(Al = 27, Mg = 24) [Ans. Al = 54.8% ; Mg = 45.2%]

52. What weight of zinc will be required to produce the same quantity of hydrogen obtained by the action of 40.5 gms. of aluminium on caustic soda solution ?

[Ans. 146.25 gms.]

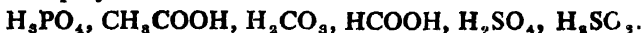
I

1. Explain and illustrate the terms acid, base and salt. Define acid, alkali and salt in the light of electrolytic dissociation. In what different ways are the acids classified? What are the informations you get from the following equations—



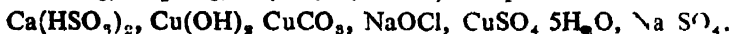
2. Define with examples :

(a) Basicity of an acid and (b) acidity of a base. What is a polybasic acid? Formulae of some acids are given below. Underline the polybasic acids.



3. What is a salt? How is it related to an acid and a base? Write what you know about normal, acid and basic salts.

Classify the following compounds as acidic, basic and normal salts.



Some salts contain replaceable hydrogen, but others do not. Explain with reasons.

4. What are oxides? How are they classified? Give one example of each type mentioning its characteristics.

5. (a) To which classes do the following oxides belong? Give reasons.

Carbon dioxide, Calcium oxide, Aluminium oxide, Nitric oxide.

(b) Which one of the following oxides reacts with HCl and NaOH separately to produce salts? And which one is indifferent to an acid or an alkali? P_2O_5 , CuO, ZnO, SO_2 , NO.

(c) Justify :

(i) BaO_2 is called barium peroxide but MnO_2 is called manganese dioxide.

(ii) Fe_2O_3 is a basic oxide, while Al_2O_3 is an amphoteric

(iii) PbO_2 is a dioxide but not a peroxide.

(iv) CO is a neutral oxide but CO_2 is an acidic oxide.

6. What is meant by hydrolysis? When a solution of sodium carbonate is added to an aqueous solution of calcium chloride, calcium carbonate is precipitated. Under similar conditions, aluminium carbonate is not precipitated when sodium carbonate is added to a solution of aluminium chloride. State the reason.

7. Define with examples : (a) equivalent weight and gm-equivalent of an acid, (b) equivalent weight and gm-equivalent of a base, (c) equivalent weight and gm-equivalent of a salt. Calculate the equivalent weight of (i) aluminium sulphate (ii) zinc nitrate, calcium carbonate silver nitrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. [Al = 27, Ag = 108, Zn = 63.38, Cu = 63.5, Ba = 137.36].

8. What is a normal solution ? How does it differ from a molar solution ? In which case the difference between the normality and molarity ceases to exist. How can an approximately N/10 solution of sulphuric acid be prepared. How would you determine its exact strength ?

9. How would you prepare 250 ml. of a $\frac{\text{N}}{10}$ Na_2CO_3 solution. What is a factor ?

10. Write notes on : (a) Normal, acid and basic salts, (b) Hydrolysis, (c) Standard solution, (d) Normal solution, (h) Indicator.

11. What is neutralisation. Give an ionic interpretation of the process. What is an indicator ? Name a suitable indicator you use in the titrations of

(a) sodium carbonate by sulphuric acid

(b) sodium hydroxide by hydrochloric acid.

Mention the colours of methyl orange, phenolphthalein and litmus in acidic, alkaline and neutral solutions.

Equal weights of NaOH and Na_2CO_3 are taken : Which will neutralise a larger quantity of an acid ?

12. What do you mean by a strong acid and a weak acid ? What actually happens during the neutralisation of a strong acid and a strong base. How is the end point of a neutralisation process determined ?

13. Complete the following sentences, choosing the appropriate term from those given within the bracket : [acidic, alkaline, neutral] Justify your choice briefly.

(a) The aqueous solution of ferric chloride is .

(b) The aqueous solution of potassium nitrate is ..

(c) The aqueous solution of copper sulphate is...

(d) The aqueous solution of sodium carbonate is. .

(e) The aqueous solution of ammonium chloride is...

14. Make critical comments on the following statements.

(a) All acids are hydrogen-compounds but all hydrogen-compounds are not acids.

(b) All alkalis are bases but all bases are not alkalis.

(c) 10 ml. of (N) Na_2CO_3 solution require 5ml. of normal hydrochloric acid solution for neutralisation, when phenolphthalein is used as an indicator.

(d) Two types of ions are eliminated when a solution of sodium hydroxide reacts with a solution of sulphuric acid.

(e) The basicity of an acid is not necessarily the number of hydrogen atoms contained in one molecule of the acid.

(f) The aqueous solution of hydrochloric acid turns blue litmus paper red but dry hydrogen chloride does not change the colour of the blue litmus paper.

(e) Upon adding sodium carbonate to an aqueous solution of ferric chloride, ferric carbonate is not precipitated.

15. Select the correct answer and mark it with \surd

(a) Acids are the substances that yield H^+ in aqueous solutions while bases yield OH^- ions. In a neutral solution,

(i) There are no H^+ ☐

(ii) There are no OH^- ☐

(iii) There are neither H^+ nor OH^- ☐

(iv) H^+ and OH^- ions are present in very small but equal in number. ☐

(b) 1M solution of hydrochloric acid conducts more electricity than 1M solution of acetic acid. This is because

(i) hydrogen chloride is highly soluble in water ☐

(ii) hydrochloric acid yields more ions than acetic acid ☐

(iii) hydrochloric acid furnishes fewer ions than acetic acid ☐

(iv) hydrochloric acid is a mineral acid while acetic acid is an organic acid. ☐

16. Indicate whether the following statements are true or false. Justify your answer.

(i) A metal always gives hydrogen when treated with an acid.

(ii) The reaction of an acid with equivalent quantity of a base gives a solution which is always neutral.

(iii) A solution of sodium chloride is neutral.

(iv) Sulphuric acid is a dibasic oxyacid.

(v) The solution obtained by dissolving 4.00 gms of NaOH in one litre of water is not exactly $\frac{N}{10}$.

II

1. Calculate the quantity of the following substances required for the preparation of :

(i) 500 ml. of 2N NaOH solution (ii) 500 ml of 5% Na_2CO_3 solution (iii) 250 ml of 0.25 (N) KOH solution (iv) 0.75 litre-

of 1.25 (M) KOH solution (v) 100 ml of (F) H_2SO_4 solution (vi) 200 ml of $\frac{\text{N}}{10}\text{AgNO}_3$ solution (vii) 500 ml of 1.25 $\left(\frac{\text{N}}{10}\right)$ Na_2CO_3 solution.

2. (a) 100 ml of caustic soda solution contain 2.5 gms of NaOH. Express the strength of the solution in terms of normality.

[Ans. 0.625 N]

(b) 25 ml of a sodium carbonate solution neutralise 10.2 ml of $\frac{\text{N}}{10}$ HCl solution. Find the strength of Na_2CO_3 solution in terms of normality and in grams per litre. [Ans. 0.0408 N ; 2.1624 gms/litre]

(c) What would be the molarity of a solution prepared by adding 400 ml of water to 100 ml of a 0.50 M solution ? [Ans. 0.1]

3. 1.3856 grams of pure Na_2CO_3 are dissolved in water and the volume of the solution is made upto 250 c.c. 24.65 c.c. of a solution of sulphuric acid is required to just neutralise 25 c.c. of the Na_2CO_3 solution. Calculate the normality of (a) Na_2CO_3 solution and (b) H_2SO_4 solution.

[Ans. Na_2CO_3 -soln. 0.1046 (N) and H_2SO_4 soln. 0.106 N]

4. Calculate the volume of 0.1 N H_2SO_4 required to neutralise a solution containing 0.125 gm of Na_2CO_3 . [Ans. 23.6 ml]

5. One gram of sodium hydroxide was dissolved in 50 c.c. of normal hydrochloric acid solution. How many c.c. of normal solution of sodium carbonate will be needed to make the solution neutral ? [Ans. 25 c.c.]

6. (a) A solution of 0.53 gm of sodium carbonate in 250 ml of water was added to 1500 ml of $\frac{\text{N}}{10}$ H_2SO_4 solution for partial neutralisation of the acid. Calculate the normality of the remaining acid solution. [Ans. 0.08 N]

(b) To 2.5 gms of pure specimen of chalk (CaCO_3), 25 ml of HCl solution were added. When evolution of gases ceased, it was found that 50% of the sample of chalk had remained undissolved. Calculate the strength of the acid in terms of normality and in gms/litre. [Ans. 1N, 36.5 gms/litre]

7. 20 c.c. of a 5% solution of caustic soda is mixed with 20 c.c. of a 5% solution of sulphuric acid. What is the normality of the resulting mixture ? [Ans. alkaline 0.115 N]

8. 1 gm of pure NaOH is mixed with 15 c.c. of molar sulphuric acid solution. Is the resulting solution neutral ? If not, find out the strength of the acidic or alkaline solution in terms of normality.

9. 50 ml of (N) H_2SO_4 are poured into 50 ml of $\frac{\text{N}}{2}$ NaOH solution. Is the resulting solution acidic or alkaline ? Calculate its strength in normality. [Ans. Acidic ; 0.25 (N)]

10. 20 c.c. of 0.45(N) NaOH are added to 30 c.c. of 0.32(N) HCl. Is the resulting solution basic or acidic? What is the normality of (a) the acidic or basic final solution and (b) the salt solution formed by neutralisation?

[Ans. Acidic; 0.012(N) acidic soln.; strength of salt soln. 0.18N]

11. 50 ml of $\frac{N}{2}$ H_2SO_4 solution are poured into 100 ml of $\frac{N}{5}$ Na_2CO_3 solution. Is the resulting solution acidic or alkaline? Calculate its normality.

[Ans. Acidic; 0.33 N]

12. The specific gravity of a sample of nitric acid is 1.5. What volume of such acid will be required to neutralise 80 gms of NaOH?

[Ans. 84 c.c.]

13. 25.5 c.c. of HCl (sp. gr. 1.10) containing 20% (by weight) HCl neutralise 21.5 c.c. of a NaOH solution. What is the normality of the NaOH solution?

[Ans. 7.2 N]

14. 100 grams of hydrochloric acid of specific gravity 1.17 contain 33.4 gms of HCl. How many litres of the acid solution of this strength would be required to neutralise 5 litres of the decinormal solution of caustic soda?

[Ans. 0.0467 litre]

15. If 25 ml of $\frac{N}{10}$ Na_2CO_3 solution ($f=1.05$) are neutralised by 19.5 ml of a solution of sulphuric acid. Calculate the strength of the acid in terms of normality and grams per litre. Calculate the volume of the acid to be diluted to one litre to make it exactly decinormal.

[Ans. 942.94 c.c.]

16. 5 c.c. of strong sulphuric acid were diluted with water and the volume was made up to 500 c.c. Upon titration, 10.2 c.c. of this diluted acid were found to neutralise exactly 22.7 c.c. of $\frac{N}{10}$ Na_2CO_3 solution. What volume of water must be added to 400 c.c. of the diluted acid to make it exactly decinormal?

[Ans. 490.2 c.c.]

17. (a) 20 c.c. of a solution of sulphuric acid neutralise 21.2 c.c. of a 3% solution of Na_2CO_3 . How would you reduce the strength of the acid solution to decinormal?

[Ans. 5 c.c. of water to 1 c.c. of acid soln.]

(b) 25 c.c. of $\frac{N}{10}$ Na_2CO_3 solution neutralise 17.5 c.c. of a solution of sulphuric acid. How much water must be added to 100 c.c. of the acid solution in order to make it exactly decinormal?

18. (a) In what proportion of volumes of two acids of strengths 0.25N and 0.4(N) respectively be mixed, so that the strength of the resulting mixed solution will be 0.32(N)?

[Ans. 8 : 7]

(b) In what volumetric proportion should an acid of 0.6 N be added to an alkali solution of strength 0.4 to make the resulting

solution (i) neutral (ii) an acidic solution of strength 0.2(N)
(iii) an alkaline solution of strength 0.2(N)

[Ans. 2 : 3 ; 3 : 2 ; 1 : 4]

19. 3.15 gms of washing soda crystals are dissolved in water and the solution is made upto 200 c.c. 20 c.c. of this solution neutralise 21.8 c.c. of N/10 sulphuric acid. What was the percentage of anhydrous sodium carbonate in the sample of washing soda ?

20. 1 gm of impure Na_2CO_3 is dissolved in water and the solution is made upto 250 c.c., 10 c.c. of this alkaline solution exactly neutralise 10.8 c.c. of $\frac{\text{N}}{10}$ HCl solution. Determine the percentage of pure Na_2CO_3 in the impure sample. [Ans. 89.438%]

21. (a) 1 gram of impure sodium carbonate is dissolved in water and the solution made up to 250 ml. To 50 ml. of this solution, 30.4 ml. of 0.15(N) HCl solution are added and the mixed solution requires for neutralisation 10 ml. of 0.12(N) NaOH solution. Determine the percentage of Na_2CO_3 in the impure sample.

[Ans. 94.04%]

(b) A 0.50 g. sample of impure calcium carbonate is dissolved in 50 ml. of 0.0985 N hydrochloric acid. After the reaction is complete, the excess hydrochloric acid requires 6.0 ml. of 0.105 N caustic soda for neutralisation. Find the percentage of calcium carbonate in the sample. [Ans. 42.94%]

22. To 50 c.c. of a solution of HCl, 25 c.c. of 0.82(N) NaOH solution were added. The excess of acid in the solution required 30 c.c. of 0.09 (N) Na_2CO_3 solution for neutralisation. Determine the normality of the acid solution and the number of grams of HCl per litre of the solution. [Cl 35.5] [Ans. 0.464 N ; 16.936 gms]

23. 3.5 c.c. of concentrated sulphuric acid (sp. gr. 1.76) is diluted with water so as to make 1 litre of the solution. 25 c.c. of this solution require 24.3 c.c. of $\frac{\text{N}}{10}$ NaOH solution for complete neutralisation. What was the percentage of the acid in the conc. sulphuric acid sample ? [Ans. 77.32%]

24. (a) 20 c.c. of an alkali solution containing 4.8 gms. of the alkali per litre require 25 c.c. of $\frac{\text{N}}{10}$ HCl for neutralisation. Calculate the equivalent weight of the alkali. [Ans. 35.4]

(b) A 6.90 M solution of KOH in water contains 30% by weight of KOH. Calculate the density of the solution. [Ans. 1.288]

25. 4.50 gms. of a dibasic acid were dissolved in water and the solution diluted to 500 ml. 20 ml. of the solution required 32 ml. of $1.25 \frac{\text{N}}{10}$ alkali for neutralisation.

Calculate the equivalent and molecular weights of the acid.

[Ans. Eq. wt. 45 ; Mol. wt. 90]

26. (a) Calculate the molecular weight of a dibasic acid, 0.45 gm. of which required 100 c.c. of $\frac{N}{10}$ NaOH solution for neutralisation. [Ans. 90]

(b) 0.75 gm. of an acid of molecular weight 90 required 16.6 c.c. of N NaOH for neutralisation. Calculate the basicity of the acid. [Ans. 2]

27. (a) The alkaline solution obtained by dissolving 1 gm. of a metal in water requires 50 ml of (N) HCl. for neutralisation. Calculate the equivalent weight of the metal. [Ans. 20]

(b) 0.3363 gm. of a metal when added to 73 c.c. of distilled water produced 190 c.c. of hydrogen gas at 27°C and 720 m.m. pressure and the solution became alkaline. Calculate the equivalent weight of the metal and the strength of the solution in terms of normality. (wt. of 1 litre of hydrogen at N.T.P. = 0.089 gm.) [Ans. Eq. wt. 22.84 ; 0.202 N]

28. (a) 3.222 gms. of a metal required exactly 98 c.c. of 10% HCl to dissolve it. What is the equivalent weight of the metal. [Ans. 12]

(b) 0.21 gm. of a metal was treated with 100 c.c. of $\frac{N}{2}$ H_2SO_4 . The metal was dissolved and the residual acid required 32.5 c.c. of N-NaOH for neutralisation. Calculate the equivalent weight of the metal. [Ans. 12]

29. One gram of the carbonate of a metal was dissolved in 25 c.c. normal HCl. The resulting liquid required 50 c.c. $\frac{N}{10}$ caustic soda solution to neutralise it completely. Calculate the equivalent weight of the carbonate. [Ans. 50.]

30. 10 c.c. of H_2SO_4 and HCl require 16 c.c. of $\frac{N}{8}$ NaOH solution for complete neutralisation. On adding excess of $BaCl_2$ solution to 20 c.c. of the above acid solution, 0.3501 gm. of $BaSO_4$ was obtained as precipitate. Calculate the gms. of HCl per litre of the acid solution.

31. A mixed solution of KOH and Na_2CO_3 required 15 c.c. of $N/20$ HCl when titrated with phenolphthalein as indicator. But the same amount of solution when titrated with methyl orange as indicator required 25 c.c. of the same acid. Calculate the amount of KOH and Na_2CO_3 in grams present in the solution. [Ans. $KOH = 0.014$ gm. ; $Na_2CO_3 = 0.053$ gm.]

32. 10 ml. of $(NH_4)_2SO_4$ were boiled with an excess of NaOH solution. The NH_3 gas evolved was absorbed in 50.0 ml. of 0.1 N

HCl. The remaining acid in the solution required 10 ml of 0.2 N NaOH solution for neutralisation. How many grams of $(\text{NH}_4)_2\text{SO}_4$ are present in a litre of the solution ? [Ans. 19.8 gm.]

33. What volume of $\frac{N}{10}$ H_2SO_4 will be required to neutralise ammonia obtained from 10.7 gms. of ammonium chloride ? [Ans. 2000 c.c.]

34. 7.5 gms. of ammonium sulphate were boiled with excess of NaOH solution and the evolved ammonia was led into 50 c.c. of (N) H_2SO_4 . The resulting solution further required 8 c.c. of 0.5 (N) NaOH for neutralisation. Calculate the percentage of ammonia in ammonium sulphate [Ans. 10.43%]

35. 10 c.c. of carbon dioxide at N.T.P. were evolved when 20 c.c. of a solution of hydrochloric acid were added to excess of powdered chalk. What is the normality of the acid ? [Ans. 0.044 N]

36. 1.48 gms. of a mixture of sodium carbonate and bicarbonate were dissolved in water and the volume made up to 250 c.c. 25 c.c. of this solution neutralised 20.85 c.c. of 0.12 (N) H_2SO_4 solution. Find the percentage composition of the mixture. [Ans. $\text{NaHCO}_3 = 28.4\%$
 $\text{Na}_2\text{CO}_3 = 71.6\%$]

37. 2 gms. of a mixture of sodium carbonate, sodium bicarbonate, and sodium chloride gave on heating 55 c.c. of carbon dioxide at N.T.P.

2 gms. of the same mixture required 32.5 c.c. of 1N HCl for complete neutralisation. Find the percentage composition of the mixture. [Ans. $\text{Na}_2\text{CO}_3 = 72.85\%$, $\text{NaHCO}_3 = 21\%$ and $\text{NaCl} = 6.15\%$]

38. Calculate the weight of pure calcium carbonate and the volume of N HCl needed to prepare 1 litre of carbon dioxide gas at 27°C and normal pressure. [Ans. $\text{CaCO}_3 = 4.052$ gms ; N HCl = 81.04 c.c.]

39. 0.25 gm. of pure calcium carbonate was found to react completely with 40 ml of dilute hydrochloric acid. Calculate the strength of the acid in terms of normality. [Ans. 0.125 N]

40. On adding excess of ferrous sulphide to 125 c.c. of a dilute solution of sulphuric acid, 560 c.c. of H_2S were obtained at N.T.P. What was the normality of the acid ? [Ans. 0.4N]

41. Calculate the volume of hydrogen chloride at N.T.P. which will be required to neutralise 60 c.c. of an alkali solution containing 4.74 gms of NaOH per litre [Ans. 0.1592 litres]

CHAPTER 7

Oxidation and Reduction.

I

1. Write notes on : (a) Oxidation (b) Reduction (c) Oxidation number (d) Electropotential series (e) Oxidising and reducing agents. Is it possible to get an oxidising agent which does not contain oxygen ?

2. Explain, according to earlier concept, the terms oxidation and reduction. Illustrate with suitable examples. Justify the statement that oxidation and reduction always take place simultaneously. Define oxidation and reduction in terms of electrons. Give examples. Comment on the inter-relation between the old and new electronic concept of oxidation and reduction.

3. Give the underlying principles of the ion-electron method of balancing redox equation. Illustrate your answer with examples.

4. What is meant by oxidation number ? How is the oxidation number of an element in its compounds determined ? State the important difference between the oxidation number and valency of an element.

5. Identify the reactants which are oxidised / reduced in the reactions represented by the following equations. Indicate also the reactions where oxidation and reduction have not occurred.

- (a) $\text{PCl}_3 + \text{Cl}_2 = \text{PCl}_5$
- (b) $\text{Si} + 2\text{KOH} + \text{H}_2\text{O} = \text{K}_2\text{SiO}_3 + 2\text{H}_2$
- (c) $\text{PbO}_2 + 4\text{HCl} = \text{PbCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$
- (d) $\text{H}_2\text{S} + 2\text{FeCl}_3 = \text{S} + 2\text{FeCl}_2 + 2\text{HCl}$
- (e) $\text{N} + \text{N} = \text{N}_2$
- (f) $3\text{CuO} + 2\text{NH}_3 = \text{N}_2 + 3\text{H}_2\text{O} + 3\text{Cu}$
- (g) $\text{KIO}_3 + 5\text{KI} + 6\text{HCl} = 3\text{I}_2 + 6\text{KCl} + 3\text{H}_2\text{O}$
- (h) $4\text{KClO}_3 = 2\text{KClO}_4 + 2\text{KCl}$
- (i) $\text{CaSO}_4 + 2\text{HCl} = \text{CaCl}_2 + \text{SO}_2 + \text{H}_2\text{O}$
- (j) $2\text{NaOH} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$

6. (a) What is the oxidation state of the underlined elements in the following species ?

NaNO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, Cl_2O_7 , H_2 , Mg , NH_4Cl , N_2H_4 , MnO_2 , KMnO_4 , K_2MnO_4

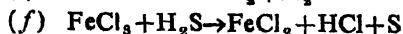
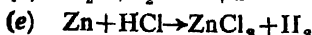
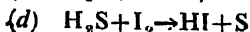
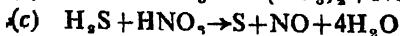
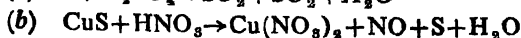
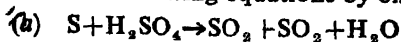
(b) What is the oxidation number of nitrogen in each of N_2O , NO , N_2O_3 , N_2O_5 , N_2 ?

(c) What is the oxidation number of sulphur in each of the compounds H_2S , SO_2 , H_2SO_3 , H_2SO_4 , S , Na_2S ?

(d) State the oxidation number of oxygen in each of the following compounds.

Na_2O_2 , Na_2O , F_2O , H_2O .

7. What do you mean by the oxidation state of an element ?
Balance the following equations by oxidation number method.



8. What is the electropotential or electrochemical series ?
Discuss the following with reference to the electrochemical series.

(a) Displacement of a metal from its salt solution by another metal.

(b) Formation and stability of metallic oxides.

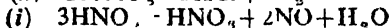
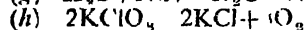
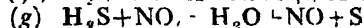
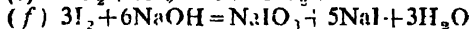
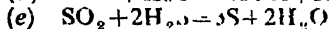
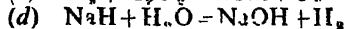
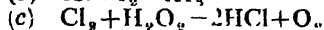
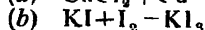
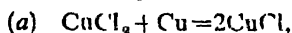
(c) All metals cannot displace hydrogen from acids. Can you cite a reaction in which hydrogen brings about an oxidation ?

9. (a) Arrange Na, Fe, Al in the order of increasing reactivity with water.

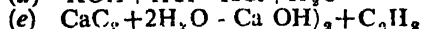
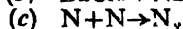
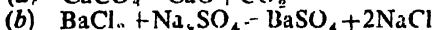
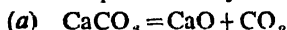
(b) Arrange Fe, Cu, Zn in the order of decreasing reducing power.

(c) How will you prepare (i) copper from copper sulphate (ii) lead from lead nitrate without the application of heat or electricity ?

10. Explain the concept of oxidation and reduction with regard to the following reactions



11. Oxidation and reduction have not taken place in the reactions represented by the following equations. Explain



12. Fill in the blank with appropriate words.

(a) Oxidation is the reaction which involves addition of — or any other — element.

(b) The reaction in which hydrogen or any electropositive element is removed is known as —.

(c) According to electronic conception oxidation is — while reduction is —.

(d) Oxidation number of an atom of an element in the free state is —.

(e) The oxidation numbers of oxygen in MnO_2 and BaO_2 are — and — respectively.

13. Explain the reasons why.

(a) Sn^{+2} and Fe^{+3} cannot coexist in the same solution.

(b) Chlorine is a stronger oxidising agent than iodine.

(c) Ag_2O and CuO have oxidising properties, while Na_2O does not possess that property.

(d) Copper cannot displace iron from ferrous sulphate solution but copper can displace silver from silver nitrate solution.

14. Oxidation is often defined as increase in the positive valency of an element due to loss of electrons and reduction as the reverse of oxidation. Explain how this statement applies in the case of the following reactions.

(a) The conversion of hydrogen ions to hydrogen molecules.

(b) The conversion of ferrous ions into ferric ions.

(c) The liberation of sulphur from hydrogen sulphide.

15. State whether the following statements are true or false.

(a) Dil. HCl oxidises metallic Fe to Fe^{++} .

(b) Copper sulphate solution cannot be kept in iron vessels.

(c) Aluminium is a stronger reducing agent than iron.

(d) Oxidation cannot occur in the absence of oxygen.

CHAPTER 8

The Gas Laws

I

1. What are the characteristics of the gaseous state of matter ?

2. State and explain the following laws in words and in the form of equations.

(a) Boyle's law (b) Charles' law (c) Dalton's law of partial pressures (d) Graham's law of diffusion.

3. Write notes on : (a) Absolute temperature (b) Partial pressure (c) Ideal gas and real gas (d) Molar gas constant.

4. Establish the relation between temperature, pressure and volume of a given mass of a gas. State the laws from which the said relation is obtained. What is the significance of absolute zero ?

How does the volume of a gas depend on it ? Is it possible to get a temperature below absolute zero ? What happens when a gas is cooled to absolute zero ?

5. What is an equation of state ? Deduce from Boyle's law and Charles' law the relation $\frac{PV}{T}$ is a constant.

6. Derive equation of state (a) for 1 mole (b) for n moles and (c) for w gms of a gas.

7. What is molar gas constant ? Why is it called a Universal Gas constant ? What are its values in different units ?

8. How can Boyles' law, Charles' law and Avogadro's hypothesis together be applied to determine the molecular weight of a gaseous compound ?

9. What is meant by partial pressure ? State Dalton's law of partial pressures. Derive an expression relating the partial pressure of a gas in a mixture to the total pressure. What is aqueous tension ? How does it influence the pressure of a gas collected over water ?

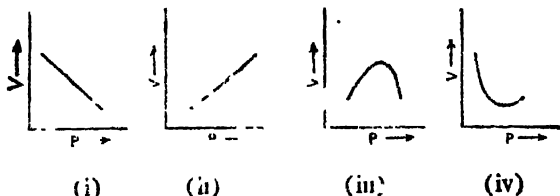
10. What is meant by gaseous diffusion ? State and explain Graham's law of diffusion. Describe an experiment to show that (i) hydrogen diffuses more quickly than air (ii) air diffuses more rapidly than carbon dioxide through the same porous wall. Arrange the gases H_2 , Cl_2 and CH_4 in the order of increasing rate of diffusion.

11. What is effusion ? State the law that governs the rate of effusion. Explain how effusion may be used to calculate vapour density or molecular weight of a gas

12. Deduce the relation between temperature, pressure and density of a given mass of a gas.

13. How does the volume of a given mass of gas change with pressure and temperature ? Explain this with the help of two familiar gas laws.

14. (a) Which one of the following graphs gives the correct relationship between the pressure and volume of a gas at constant temperature ?



(b) Show a graphical representation of a gas obeying Boyle's law with volume (v) along X-axis and inverse of the pressure ($\frac{1}{P}$) along Y-axis.

15. What will be the nature of graph in the following cases :—

- (a) 'PV' plotted against 'P' at constant temperature
- (b) 'V' plotted against 'T' at constant pressure.

16. Mark the correct answer as \surd . Non-reacting gases tend to mix with each other to form homogeneous mixture. This phenomenon is called

- (a) synthesis ☐
- (b) addition ☐
- (c) diffusion ☐
- (d) effusion ☐

II

1. A quantity of gas occupies 240 c.c. at 750 m.m. pressure of mercury. What volume will it occupy at 600 m.m. pressure, temperature remaining constant ? [Ans. 300 c.c.]

2. A volume of air at a certain temperature is compressed to $\frac{1}{3}$ th its original volume. What multiple of the former pressure will be the new pressure, temperature remaining constant ? [Ans. 6]

3. A balloon contains 1250 ml. of a gas at 760 m.m. pressure. The balloon is taken to the top of a mountain where the pressure is found to be 720 m.m. of mercury. What will be the change in volume of the balloon at the top of the mountain, temperature remaining constant ? [Increase of vol by 60 ml.]

4. At what depth in a pond will a bubble of air have one half of the volume it will have on reaching the surface ? (Barometric height 76 cm. of Hg, density of mercury 13.6, temperature of water in the pond 15°C). [Ans. 1033.6 cm.]

5. A volume of gas together with a marble ball measures 150 c.c. at 760 m.m. pressure. On raising the pressure to 1000 m.m., the combined volume becomes 116.4 c.c. What is the volume of the marble ball ? Temperature remains constant [Ans. 10 c.c.]

6. A given mass of gas occupies a volume of 240 ml. at a pressure of 1.25 atmospheres ; how much would be the volume change if the pressure was altered to 0.75 atm. at the same temperature ? What would be the volume of double the given mass of gas at the latter pressure ? [Ans. Increase of pressure = 160 ml. ; Double the volume]

7. Mercury is poured into a tube closed at one end until it reaches a point 2.5 cm. from the open end. The tube is then inverted and placed in a vertical position with the lower end in a trough of mercury. It is then found that air fills 38 cm. of the tube while a column of mercury 70 cm. long is sustained below it. Find the atmospheric pressure. [Ans. 74.9 cm.]

8. 50 c.c. of hydrogen at N.T.P. were confined in a tube of cross section 1.2 sq. cm. and standing in a trough of mercury, the volume of which stood at a height of 15 cms. The pressure was

now changed to 750 m. m. and the temperature to 31°C . Find the length of the column of tube containing the gas.

9. One litre of a gas is measured at 27°C . At what temperature will its volume be two litre., the pressure remaining constant?

[Ans. 600°A or 327°C]

10. How much air will escape from the flask of one litre capacity if it is warmed from 25°C to 35°C , the pressure remaining constant?

[Ans. 33.56 c.c.]

11. Some amount of nitrogen occupies 50 c.c. at 50°C . If the pressure remains unchanged, what will be the volume of the same amount of the gas at -50°C ?

[Ans. 34.5 c.c.]

12. A gas expands from 1 litre to 1.128 litres due to a rise of temperature from 0°C to 35°C at constant pressure. From this, calculate the value of absolute zero (in centigrade scale).

[Ans. -273.4°C]

13. 304 c.c. of a dry gas are collected under a pressure of 750 m.m. and at 27°C . Find the volume of the gas at N.T.P.

[Ans. 273 c.c.]

14. A given mass of a gas occupies a volume of 2.5 litres at 0°C and 76 cm pressure of mercury. Find its volume at 546°C and 150 cm. pressure of mercury.

[Ans. 3.8 litres]

15. Calculate the pressure when 22.4 litres of oxygen at 0°C and 1 atm pressure are led into an evacuated vessel of 50 litres capacity at 15°C .

[Ans. 35.41 m.m.]

16. Calculate the diminution in size of a dry balloon of which the volume is 450 c.c. at 12°C and 750 m.m. pressure, when taken to the bottom of a mine where the pressure is 765 m.m. and the temperature 5°C .

[Ans. 16.3 c.c.]

17. A quantity of a gas together with a piece of glass measures 100 c.c. at 27°C . When the pressure is doubled and the temperature raised to twice the above figure, the combined volume is found to be 59.3 c.c. Find the volume of the piece of glass.

[Ans. 10.55 c.c.]

18. A flask can bear pressure upto 16 atmospheres. It is filled with chlorine at 10°C and 764 m.m. It is now heated till the flask explodes. At what temperature does the explosion take place?

[Ans. 177.429°C]

19. At 0°C and a pressure of 2 atm, 350 ml. of a diatomic gas weight 1 gm. Calculate the actual weight of an atom of the gas in grams.

[Ans. 2.6571×10^{-25}]

20. (a) Find out the volume occupied by 4 grams of oxygen at 27°C and 760 mm pressure.

[Ans. 6.15 litres]

(b) 2 grams of oxygen are confined in a 2-litre vessel by a pressure of 1.21 atm. What is the temperature of the gas at $^{\circ}\text{C}$?

[Ans. 200°C]

21. What volume at 27°C and 740 mm. pressure will be occupied by 1.7 gms. of ammonia gas ?

22. Calculate the number of moles present in 10 litres of oxygen at 27°C and 57 cm. of mercury. [Ans. 0.305 mole]

23. The density of hydrogen at N.T.P. is 0.09 gms. per litre. What is the density at 15°C and 750 mm. pressure ?
[Ans. 0.084 gm/litre]

24. Calculate the temperature at which air possesses a density equal to that of hydrogen at 0°C . (Density of air = 14.4)
[Ans. 3658.2°C]

25. The density of air at 0°C and 76 cm. pressure is 1.293 per litre. Calculate the density of air at 27°C and 64 cm. pressure
[Ans. 0.991 gm/litre]

26. (a) At a pressure of 752 mm., a mass of 0.324 gm. of a gas occupies 280 ml. at 23°C . At what temperature will 1.00 gm. of the same gas occupy exactly 1 litre at 1 atm. pressure ? [Ans. 73°C]

(b) At 10°C and under a pressure of 2 atmospheres, 3.362 gms. of a gas occupy a volume of 1.224 litres. At what pressure will 0.436 gm. of the same gas occupy exactly 300 ml. at 25°C ?
[Ans. 1.22 atms.]

27. (a) 2 gms. of oxygen are confined in a 2 litre vessel by a pressure of 1.21 atms. What is the temperature of the gas at $^{\circ}\text{C}$?

(b) How many molecules are there in one millilitre of a perfect gas at a pressure of 1 cm. at 27°C ? [Ans. 3.2×10^{17}]

(c) Applying the equation of state, find the volume occupied by 5×10^{23} molecules of a gas at N.T.P.

(d) Oxygen is present in a 1-litre flask at a pressure of 7.6×10^{-10} m.m. of Hg. Calculate the number of oxygen molecules in the flask at 0°C . [Ans. 2.69×10^{10}]

28. 3.2 gms. of sulphur when vaporised at 450°C and 720 mm. pressure occupy a volume of 780 ml. What is the molecular formula of sulphur under such condition ? [Ans. S_8]

29. 33.6 c.c. of phosphorus vapour weigh 0.0625 gm. at 546°C and 76 cm-Hg pressure. What is the molecular weight of phosphorus ? How many atoms are there in one molecule of phosphorus vapour ? [Ans. 125 ; 4.0 (approx.)]

30. How much air at 27°C and 750 mm. pressure will be required for complete combustion of 60 gms. of a hydrocarbon containing 80% of carbon and 20% of hydrogen. Air contains 21% of oxygen by volume.

31. What volume of oxygen gas at N. T. P. is necessary for complete combustion of 20.0 litres of propane (C_3H_8) measured at 27°C and 760 mm. of mercury. [Ans. 91 litres]

32. (a) The weight of 380 ml. of a gas is 0.455 gm. at a temperature of 27°C and a pressure of 800 mm. Determine the molecular weight of the gas. [Ans. 28.0]

(b) One gram of an alloy of aluminium and magnesium reacts with excess of hydrochloric acid to form aluminium chloride, magnesium chloride and hydrogen. The hydrogen, collected over mercury at 0°C, occupied 1200 ml. at 699 mm. of Hg. What is the composition of the alloy ?

(c) Air contains 21% by volume of oxygen and 79% by volume of nitrogen. Calculate the density of air in grams per litre at 27°C and 760 mm pressure.

[Ans 1.171 gms/litre]

33. A certain gas occupies 0.418 litre at 27°C and 740 mm. of Hg ?

(i) What is its volume at N.T.P. ?

(ii) If the same gas weighs 3.0 gms., what is its molecular weight ?

(iii) If we increase the weight of the gas to 7.5 gms. in the same vessel (i.e., 0.418 litre capacity) and the temperature is lowered to 280 K what would be its pressure now ?

[Ans. 0.3703 litre ; 181.4 ; 2.272 atms.]

34. 0.44 gm of a colourless oxide of nitrogen occupies 224 ml. at 1520 mm. Hg and 273°C. Identify the compound. How much in gram does one molecule of this compound weigh ?

[Ans. N_2O ; 7.309×10^{-22} gm.]

35. A compound contains 10.05% carbon, 0.84% hydrogen and 89.1% chlorine. Its density in the gaseous state at 150°C and 760 mm pressure is 3.43 gm/litre. What are its empirical formula and molecular formula ?

36. At 25°C partial pressures of the constituent gases in a gas mixture are 430 mm., 100 mm., 80 mm., 70 mm., 27 mm. and 10 mm. of mercury. Find the total pressure of the mixture.

[Ans. 717 mm. of Hg.],

37. A sample of dry air has the following composition :

Nitrogen	76.03%
Oxygen	20.9%
Argon	0.9%
Carbon dioxide	0.4%

Determine the partial pressure of each of the constituents of air.

[Ans. N_2 —591.46 mm, O_2 —158.4 mm., Ar—6.8 mm. and CO_2 —0.3 mm.]

38. A volume of 0.5 litre of nitrogen measured at 25°C and at 700 mm. and 1 litre of oxygen at a pressure of 600 mm., are passed into an empty vessel whose capacity is 2 litres. What is the total pressure of the mixture in the vessel at the same temperature.

[Ans. 475 mm.]

39. Dry air contains by volume 1 part of oxygen and 4 parts of nitrogen. The pressure of air is 76. cm. Calculate the partial pressures of oxygen and nitrogen.

[Ans. p_{O_2} = 15.2 cm. ; p_{N_2} = 60.8 cm.]

40. 45 gms. of electrolytic gas is contained in a 60 litre gas-holder at 0°C . What is the partial pressure of each constituent ? What is the total pressure ?

[Ans. $p_{\text{H}_2} = 0.933 \text{ atm.}$, $p_{\text{O}_2} = 0.467 \text{ atm.}$, 1.4 atm.]

41. 190 ml. of a gas, collected over water at 25°C and a pressure of 740 mm of mercury. Calculate the volume the dry gas would occupy at N.T.P. [Vapour pressure of water at 25°C is 23.8 mm.]

[Ans. 179.0 ml.]

42. 0.218 gm. of magnesium gave 218.2 c.c. of moist hydrogen at 17°C and 745 mm. from HCl. Find the weight of the metal that will liberate 11.2 litres of hydrogen at S.T.P. (Aqueous tension at 17°C is 14.5 mm.)

[Ans. 12.21 gm.]

43. At standard conditions, a gas mixture of three gases A, B and C, contains 77% of A, 21% of B and 1.5% of C by volume. Determine the partial pressures of A, B and C.

44. A two litre glass vessel contains nitrogen and water vapour in equimolecular proportions at a pressure of 10^{-3} mm. mercury at 303°K . Calculate—

(i) the number of moles of nitrogen and water vapour present and

(ii) the total mass of the gaseous mixture when the mixture is cooled to 50°C

[Ans. No. of moles of N_2 and H_2O (gas) = 5.29×10^{-8} moles ; Total mass of the mixture = 2.43×10^{-6} gm.]

45. The total pressure of a mixture of 1 gm of hydrogen and 10 gms of carbon monoxide is 800 mm. Find the partial pressure of each of the gases in the mixture.

[Ans. $p_{\text{H}_2} = 466.7 \text{ mm.}$; $p_{\text{CO}} = 333.3 \text{ mm.}$]

46. Equal volumes of hydrogen and nitrogen diffuse through a porous wall in 16 and 60 seconds respectively. Calculate the molecular weight of nitrogen.

47. 1 litre of nitrogen weighs 1.25 gms. whereas 1 litre of chlorine weighs 3.21 gms. Which of the two gases diffuse faster ? Determine the relative rates of diffusion of the two gases.

[Ans. 1 : 1.16]

48. 180 ml of a hydrocarbon diffuse through a porous membrane in 15 minutes while 120 ml of sulphur dioxide, under identical conditions, diffuse in 20 minutes. What is the molecular weight of the hydrocarbon ?

[Ans. 16]

49. Find the ratio of the rates of diffusion of methane (CH_4) and sulphur dioxide (SO_2).

[Ans. 1 : 2]

→ 50. In an experiment, it was found that 500 c.c. of a gas A diffused through a hole into a vacuum in the same time as 620 c.c. of air. Calculate the density of A relative to air. (Air is 14.4 times heavier than hydrogen)

[Ans. 1.54]

51. Oxygen is mixed with another gas. On diffusion, the mixture produces another mixture containing 61.77% of oxygen. What is the molecular weight of the other gas ? [Ans. 83.12]

52. The relative amounts of the two gases produced by diffusion of a mixture of the gases are in the ratio of 1 : 3.5. If the density of the second gas is 0.001246 gm/cc, find the molecular weight of the first gas. [Ans. 2.29]

53. The time taken for a certain volume of ozone containing 20% of oxygen (by volume) to stream through a small hole was 175 seconds. Under exactly the same conditions, an equal volume of oxygen took 168 seconds. Calculate the density of ozone.

54. 50 c.c of hydrogen take 10 minutes to diffuse out of a vessel. How long will 40 c.c. of oxygen take to diffuse under similar conditions ? [Ans. 32 minutes]

55. The time taken for a certain volume of gas to stream through a small hole was 1.44 min ; under exactly the same conditions, an equal volume of oxygen took 1.80 min to pass through. Calculate the approximate density of the gas relative to hydrogen. [Ans. 10.2]

56. The molecular weight of carbon dioxide is 44. Calculate the molecular weight of ozone if 96 c.c. of it diffuse through an orifice from which under similar conditions 100 c.c. of carbon dioxide will pass in the same time. [Ans. 47.74]

57. If the relative rates of diffusion of oxygen and sulphur dioxide be 14.4 and 100, find the density and molecular weight of sulphur dioxide. [Ans. 31.99 ; 63.98]

58. 25 c.c. of oxygen were found to diffuse out of a porous vessel in 100 seconds. What volume of carbon dioxide would diffuse in the same time under the same conditions ? [Ans. 21.32 c.c.]

59. A gaseous hydrocarbon contains 14.28% hydrogen. The rates of diffusion of hydrogen and this hydrocarbon, are 1 : $\sqrt{14}$. Find the formula of the hydrocarbon. [Ans. C_2H_4]

CHAPTER 9

Chemical equilibrium

I

1. Explain, with examples the meaning of a reversible chemical reaction. What are its characteristics ? "All chemical reactions are reversible" Comment on the statement.

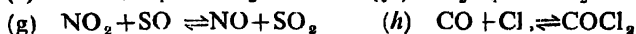
2. What do you understand by chemical equilibrium ? Show how a state of chemical equilibrium is attained. What are the properties of the equilibrium state ?

3. State and explain the law of mass action. What is active mass of a substance ? Derive an expression for the equilibrium

constant of a homogeneous reversible reaction in the most general case. Deduce a relation between K_p and K_c .

4 State Le Chatelier's Principle. Apply this principle in predicting the influence of temperature, pressure and addition of any of the substances taking part in the reaction upon some familiar reaction equilibria

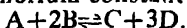
5. What is understood by a chemical system in equilibrium? Why is such equilibrium considered as dynamic? Formulate the equilibrium constant K_p and K_c for each of the following reactions.



6. Discuss the effect of increase of pressure on the following reactions.



7. (a) State and explain the law of mass action and deduce an expression for the equilibrium constant for the reaction

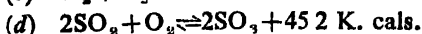
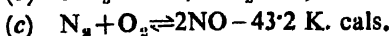
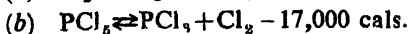


What will be effect of (a) increasing the pressure, (b) increasing the temperature on the equilibrium if the reaction is exothermic?

(b) The reactions $2CO + O_2 \rightleftharpoons 2CO_2$ and $CaCO_3 \rightleftharpoons CaO + CO_2$ are not complete. How can the reactions be brought to completion?

8. Write notes on : (a) Le Chatelier's Principle (b) Dynamic equilibrium (c) Active mass (d) Law of mass action.

9. State and explain Le Chatelier's Principle in case of a dynamic chemical equilibrium. Illustrate its application to determine the influence of temperature and pressure on the condition of equilibrium in the following cases.



10. Discuss the application of Le Chatelier's Principle in the working conditions of some important industrial processes.

11. (a) Chemical reactions are more or less reversible in nature but under some conditions they may go almost upto completion. Discuss the statement with suitable examples.

(b) State how the following reaction can be made to proceed almost upto completion :



12. Mark the correct answer by \surd

(a) In a reversible reaction, $2A + B \rightleftharpoons C + D$ the equilibrium constant (K) is given by the expression

- (i) $\frac{[A]^2 \times [B]}{[C] \times [D]}$ ☐
- (ii) $\frac{2[A] \times [B]}{[C] \times [D]}$ ☐
- (iii) $\frac{[C] \times [D]}{[A]^2 \times [B]}$ ☐
- (iv) $\frac{[C] \times [D]}{2[A] \times [B]}$ ☐

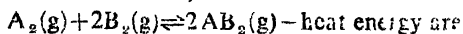
(b) For the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, The equilibrium constant K_p changes with

- (i) total pressure ☐
- (ii) catalyst ☐
- (iii) the amounts of H_2 and I_2 present ☐
- (iv) temperature ☐

(c) For the reaction, $2HI \rightleftharpoons H_2 + I_2$, the relation between K_p and K_c is

- (i) $K_p \cdot K_c = 1$ ☐
- (ii) $K_p = K_c$ ☐
- (iii) $K_p = K_c \cdot V$ ☐
- (iv) $K_p + 1 = K_c$ ☐

(d) Favourable conditions for the maximum yield of the product AB_2 in the reaction,



- (i) high pressure, high temperature ☐
- (ii) high pressure, low temperature ☐
- (iii) low pressure, high temperature ☐
- (iv) low pressure, low temperature ☐

(e) In a reversible reaction, a catalyst

- (i) increases the rate of the forward reaction only ☐
- (ii) increases the rate of the forward reaction to a greater extent than that of the reverse reaction ☐
- (iii) increases the rate of forward reaction and decreases the rate of reverse reaction ☐
- (iv) increases the rates of forward and reverse reactions equally ☐
- (v) increases the rate of forward reaction and stops the reverse reaction ☐

II

1. At 500 C, 1.04 gm of hydrogen and 12.060 gm of iodine are in equilibrium with 5.058 gm of hydrogen iodide. Calculate the equilibrium constant. [Ans. 63.2]

2. Calculate K_p when 69% of HI by mole is found to be present at equilibrium during dissociation of HI. [Ans. 0.178]

3. If the value of K be 50.21, for the reaction $H_2 + I_2 \rightleftharpoons 2HI$, how much HI would be present at the equilibrium if we start with 5.30 moles of iodine and 7.94 moles of hydrogen? [Ans. 9.72 moles]

4. If a mixture of 3 moles of hydrogen and 1 mole of nitrogen react under a constant pressure of 100 atms. to form at equilibrium 0.5 mole of ammonia. Calculate K_p for the reaction, $\frac{3}{2}H_2 + \frac{1}{2}N_2 \rightleftharpoons NH_3$, at this temperature.

5. At 25 C, 1 mole of acetic acid and 1 mole of ethyl alcohol were mixed. At equilibrium, 33.3% of the acid remained unreacted. Calculate K_c . [Ans. 4]

6. A mixture of 3 gm. moles of ethyl alcohol and 1 mole of acetic acid are allowed to come to equilibrium. If the equilibrium constant for the reaction is 4, how much ethyl acetate is present at the equilibrium? [Ans. 0.91 gm.-mole]

7. At 250 C, the equilibrium constant for the reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, $K_p = 1.8$. Calculate the pressure in twopheres necessary to obtain a 50% dissociation of PCl_5 . [Ans. 5.4 atms]

8. 2 NO is obtained at equilibrium produced by the reaction $N_2 + O_2 \rightleftharpoons 2NO$ when started with 1 mole of N_2 and 1 mole of O_2 . Find out K_p . [Ans. 0.00167]

9. A mixture of 6.22 moles of hydrogen and 5.71 moles of iodine was heated at 357 C and the amount of free iodine in the equilibrium mixture was found to be 0.91 mole. Calculate the equilibrium constant for the reaction $H_2 + I_2 \rightleftharpoons 2HI$. [Ans. 0.0140]

10. 2 gm-molecules of phosphorus pentachloride were heated in a closed two-litre vessel. When the equilibrium was attained, it was found that 60 per cent of the phosphorus pentachloride remained undissociated. Calculate the equilibrium constant [Ans. 0.267]

11. Ammonia under a pressure of 15 atm at 27 C is heated to 347 C in a closed vessel in the presence of a catalyst. Under these conditions, ammonia is partially decomposed according to the equation : $2NH_3 \rightleftharpoons N_2 + 3H_2$

The vessel is such that the volume remains effectively constant, whereas the pressure increases to 50 atms. Calculate the percentage of NH_3 actually decomposed.

Group B**CHAPTER 1 : Oxygen and Hydrogen**

1. Write notes on : (a) Catalyst and Catalysis (b) Allotropy (c) Nascent state and nascent hydrogen (d) Occlusion (e) Silent electric discharge (f) Hard water and soft water (g) Permutit (h) Hydrides.

2. What is the name of the gas which is obtained by heating mercuric oxide in a hard glass test tube ? How is the gas prepared from potassium chlorate in the laboratory ? Why is manganese dioxide mixed with potassium chlorate ?

What are the precautions to be taken during the laboratory preparation of oxygen ? State the important uses of oxygen.

3. How would you prove experimentally that each of the following compounds contains oxygen ?

(a) Lead nitrate (b) Sulphuric acid (c) Nitric acid (d) Hydrogen peroxide ?

The word oxygen means "acid producer". Give two examples to show that name as given to oxygen is justified and two other examples to show that the name is a misnomer.

4. Describe (with a sketch of the apparatus used) the laboratory method of preparation of oxygen. How is oxygen obtained from the air ? How would you identify this gas ? State the conditions under which oxygen reacts with the following non-metals and metals.

(a) hydrogen (b) nitrogen (c) sulphur (d) phosphorus (e) sodium (f) magnesium.

5. How is hydrogen prepared in the laboratory ? How is the gas collected and purified ? What are the precautions to be adopted during the preparation of the gas ? State some of its important uses. How can hydrogen be converted into water without using oxygen ?

6. Make a neat diagram of Kipp's apparatus and give a brief description. Explain how it is used for getting a ready and controlled supply of hydrogen in the laboratory.

7. Describe how hydrogen may be prepared and collected by decomposition of water (i) by a metal at ordinary temperature (ii) by a metal at red heat (iii) without the application of chemicals.

State the physical and chemical properties of hydrogen. Describe experiments to show that (a) water is formed when hydrogen is burnt in oxygen (b) hydrogen is lighter than air (c) hydrogen is a reducing agent (d) nascent hydrogen is more powerful reducing agent than ordinary hydrogen.

8. What are hard water and soft water ? What is the hardness of water due to ? What are the causes of temporary hardness and permanent hardness ?

Describe one effective method of removing both temporary and permanent hardness of water.

Mention with reasons whether the following samples of water are hard or soft.

(a) River water, (b) Rain water, (c) Spring water, (d) Well-water, (e) Distilled water. (f) Water obtained by melting ice.

9 **Why is hard water unsuitable for laundry boiler and drinking purposes? Impure, hard water taken from a natural source is purified separately by distillation and by the permutit process. Which of the samples of water thus obtained will be purer? Does the water become hard if a little zinc sulphate or potassium nitrate is added to it?**

10 **Write a short account of the different methods of removal of hardness of water. State the equations where possible. How can you obtain water of the quality of distilled water without distillation?**

11. **State with equations, the conditions under which water reacts with the following substances: (a) sodium (b) calcium (c) iron (d) carbon (e) lime (f) calcium carbide (g) sodium peroxide (h) phosphorus pentoxide (i) magnesium.**

12. **How would you test if a sample of colourless liquid is water? Prove that water is a compound.**

13. **How would you determine the volumetric composition of water by an analytical method and a synthetic method?**

14. **Describe Duma's experiment on the composition of water by weight. Mention the precautions which should be taken.**

15. **Water contains hydrogen and oxygen in the ratio of 1 : 8 by weight. Prove the truth of the statement by two experiments.**

16. **How would you collect the gases obtained by passing electricity through pure water containing a little dilute sulphuric acid. Give a neat sketch of the apparatus you would use. How are these gases identified? State the conditions under which they recombine to form water.**

17. **How is hydrogen peroxide prepared in the laboratory? How is it purified? Describe its important properties and uses. Hydrogen peroxide reacts as an oxidising agent and a reducing agent. Discuss with suitable examples.**

18. **Give a brief account of the different methods of preparation of hydrogen peroxide. State what happens when a dilute aqueous solution of hydrogen peroxide is evaporated on a water bath. Describe experiments to show that (a) hydrogen peroxide is an oxidising agent (b) hydrogen peroxide is a reducing agent (c) hydrogen peroxide liberates oxygen on heating (d) hydrogen peroxide possesses acidic properties.**

Which type of substances are reduced by hydrogen peroxide?

19. Giving necessary equations, discuss the action of hydrogen peroxide on the following substances—

- (a) acidified potassium permanganate solution (b) lead sulphide (c) acidified potassium iodide solution (d) ozone (e) silver oxide.
How is the strength of hydrogen peroxide expressed? How will you confirm that a given liquid is hydrogen peroxide?

20. Describe a method of preparation of ozone in the laboratory. Give a sketch of the apparatus used. Give a brief account of the physical and chemical properties of ozone. Mention some of the important uses of ozone.

21. (a) How can you prove that ozone is an allotropic modification of oxygen? (b) Why is ozone chemically more reactive than oxygen?

Compare the physical and chemical properties of ozone with those of hydrogen peroxide.

How is the presence of ozone detected?

22. Complete and write balanced equations.

- (a) $\text{H}_2\text{O}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + \dots \rightarrow \text{Cr}_2(\text{SO}_4)_3 + \dots + \dots + \text{H}_2\text{O}$
(b) $\text{KNO}_3 \rightarrow \text{KNO}_2 + \dots$ (c) $\text{HNO}_3 \rightarrow \dots + \text{H}_2\text{O} + \text{O}_2$
(d) $\text{H}_2\text{O}_2 + \text{KMnO}_4 + \dots \rightarrow \text{K}_2\text{SO}_4 + \dots + \text{O}_2 + \dots$
(e) $\text{Fe} + \text{H}_2\text{O} \rightarrow \dots + \text{H}_2$ (f) $\text{NaH} + \text{H}_2\text{O} \rightarrow \dots + \dots$
(g) $\text{AlN} + \text{H}_2\text{O} \rightarrow \dots + \dots$
(h) $\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \dots + \text{H}_2\text{O}$
(i) $\text{KI} + \dots + \text{H}_2\text{O}_2 \rightarrow \text{I}_2 + \text{KCl} + \dots$ (j) $\text{PbS} + \text{O}_3 \rightarrow \dots + \dots$

23. Explain, with equations where necessary, the changes taking place when—

(a) The product of combustion of sodium in air is treated separately with water and dil. sulphuric acid. (b) Lead nitrate, silver nitrate, potassium dichromate, potassium permanganate are heated separately. (c) Potassium chlorate mixed with manganese dioxide is heated. (d) Two gas jars one containing nitric oxide and the other hydrogen are exposed to air. (e) Ozone and ethylene are made to interact with each other. (f) Sulphur dioxide solution is kept exposed in air. (g) Ozone is passed into ferrous sulphate solution acidified with sulphuric acid.

24. Discuss how you would separate (a) hydrogen from water gas (b) oxygen from a mixture of hydrogen and oxygen (c) oxygen from a mixture of oxygen and nitrogen (d) oxygen from a mixture of ozone and oxygen.

You are given three jars of colourless gases containing hydrogen, oxygen and nitric oxide. How would you identify each by a single experiment on each?

25. State the reasons why—

(a) Conc. sulphuric acid is not used for the preparation of hydrogen by the action of zinc. (b) Copper cannot liberate hydrogen from dil. sulphuric acid (c) Hydrogen is not generally obtained from nitric acid by the action of metals. (d) Soap does not easily form lather with hard water (e) Hard water should not be used in a boiler. (f) The colour of a solution of ferric chloride acidified with dil. sulphuric acid remains unchanged when hydrogen from a Kipp's apparatus is passed through it, but the acidified ferric chloride solution becomes colourless if a piece of granulated zinc is added to it. (g) Hydrated barium peroxide not anhydrous barium peroxide is used in the preparation of hydrogen peroxide.

(h) Concc H_2SO_4 is not used in the preparation of H_2O_2 .

26. Fill in the blanks with appropriate words.

(a) The absorption of hydrogen by palladium is commonly known as...

(b) In the thermal decomposition of potassium chlorate, manganese dioxide acts as a . .

(c) Temporary hardness of water can be removed by ..

(d) Ozone is absorbed by---

27. Describe the experiments to illustrate :

(a) A catalyst can influence the rate of a chemical reaction.

(b) Molecular hydrogen and nascent hydrogen differ in properties.

(c) Water is a compound of hydrogen and oxygen.

(d) Oxygen can be prepared from one of its compounds at ordinary temperature.

28. Indicate whether the following statements are *true* or *false*.

(a) Ozone is a stable compound (b) Oxygen is an allotropic modification of ozone (c) Hard water should never be used for drinking purpose (d) Oxygen is more reactive than ozone (e) Oxygen is an isotope of ozone (f) Hydrogen peroxide is a hydride (g) Hydrogen peroxide is an acid (i) There are substances other than oxygen which support combustion.

29. (a) Calculate the weight of CaO required to remove the hardness of 10,00,000 litres of water containing 1.62 grams of calcium bicarbonate per litre. [Ans. 5.6×10^8 gm.]

(b) Find the hardness of a sample of water containing 0.001 mole of MgSO_4 per liter.

(c) A sample of hard water contains 20mg of Ca^{++} ions per litre. How many milliequivalents of Na_2CO_3 would be required to soften 1 liter of the sample ?

[Ans. 1 milli equivalent of Na_2CO_3]

30. 50 ml of a hydrogen peroxide solution give on heating 2 liters of oxygen at N. T. P. Find the volume strength of the solution and the strength in percent. [Ans. 39.99 volume ; 12.14%]

31. 100 ml of ozone at N.T.P. were passed through 100 ml. of '10 volume' hydrogen peroxide solution. What is the volume strength of the latter after the reaction ? [Ans. 9.5 volume.]

CHAPTER 2 :

Air and Nitrogen

1. Both air and nitric oxide contain oxygen and nitrogen ; show that one of them is a mechanical mixture and the other is a chemical compound.

2. Write down the names of the constituents of air. State their utility. Describe an experiment to show that air contains mainly two gases in the ratio of 1 : 4 and one of the gases supports combustion and the other does not.

3. "Air is a mixture and not a compound". What are the facts to justify this statement ?

4. How is nitrogen prepared and dried in the laboratory ? State some reactions in support of its chemical reactivity. Write some important uses of nitrogen. What is nitrolim ?

5. Describe one method each for the preparation of nitrogen from (a) air (b) ammonium nitrite (c) ammonia (d) nitric acid.

Nitrogen obtained from air is found to be heavier than that prepared from ammonium nitrite. Explain the reason.

6. How and under what conditions does nitrogen react with the following substances ?

(a) Magnesium (b) Aluminium (c) Hydrogen (d) Calcium carbide (e) Oxygen

Write the names of the products and discuss the action of water on each of them.

7. (A) State giving equations and mentioning the visible change, if any, what happens when :—

(i) a concentrated solution of sodium nitrate and ammonium chloride is heated

(ii) a piece of magnesium wire is burnt in air and the products are boiled with water

(iii) nitrogen is passed through heated calcium and the product is made to react with water.

(B) Complete and balance the equation if necessary.

(i) $\text{CaC}_2 + \dots = \text{CaCN}_2 + \dots$

(ii) $\dots + \text{NH}_3 = \text{N}_2 + \dots$

(C) You are given two jars of colourless gases containing nitrogen and nitric oxide. How would you identify each by a single experiment on each ?

(D) Write notes on : Nitrogen Cycle.

CHAPTER 3 : The non-metals, Carbon, phosphorus, Sulphur and Halogens

1. Name the different allotropes of carbon. Give a brief account of the properties and uses of each of them. How is graphite prepared artificially? Prove experimentally that different allotropes of carbon consist of the same element.

2. How is phosphorus obtained from phosphate mineral or bone ash? How can white phosphorus be converted into red phosphorus and vice versa?

Give two examples showing the reducing property of phosphorus. Give equations. Does phosphorus occur free in nature?

Compare and contrast the properties of phosphorus with those of nitrogen.

3. State with equations, how phosphorus reacts with (a) caustic soda solution, (b) copper sulphate solution, (c) Chlorine and (d) nitric acid. Give a comparative account of the properties of white and red phosphorus.

4. Give a concise account of two methods of extraction of sulphur from natural source. State some of the important uses of sulphur. Discuss the statement that sulphur shows allotropy. How can you prove that rhombic and monoclinic sulphur are the same element?

5. How is pure chlorine (free from hydrogen chloride) prepared in the laboratory? Can chlorine be prepared with the help of a Kipp's apparatus? State the physical and chemical properties of chlorine. Explain with equations, the reaction of chlorine with the following.

(a) Caustic soda solution, (b) Sulphur dioxide solution, (c) Slaked lime, (d) Hydrogen sulphide, (e) Carbon monoxide (f) Ammonia solution.

Mention the principal uses of chlorine.

6. Describe briefly the methods used in the laboratory for the preparation of bromine and iodine. Show that bromine and iodine show similarities in chemical reactions. State some of the uses of bromine.

7. State with equations, the reactions of iodine with the following reagents.

(a) Water, (b) Alkali solution, (c) Potassium iodide solution, (d) Nitric acid.

8. What are halogens? Give a comparative account of the properties of chlorine, bromine and iodine

9. How will you prove that,

(a) calcium phosphate contains phosphorus,

(b) hydrochloric acid contains chlorine,

- (c) chlorine is a stronger oxidising agent than iodine,
- (d) white phosphorus and red phosphorus are different forms of the same element,
- (e) potassium chlorate contains chlorine and oxygen,
- (f) activated charcoal is a good adsorbent.

10 Answer as directed—

(a) You are given a black substance which is either manganese dioxide or powdered carbon. How will you proceed to identify the substance?

(b) Oxygen is prepared by heating potassium chlorate with manganese dioxide. Conc. hydrochloric acid on being heated with manganese dioxide gives chlorine. What is the role of manganese dioxide in both the reactions?

(c) A brown solid is either graphite or iodine. How can you identify the solid?

(d) How would you free traces of chlorine from oxygen and detect the presence of traces of chlorine in a sample of hydrogen chloride?

(e) How would you separate the constituents of a mixture of potassium iodide and iodine?

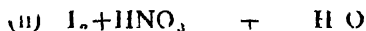
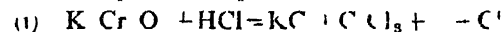
(f) _____ emits a green glow visible in the dark. Fill up the blank correctly with either white phosphorus or sulphur.

(g) Lead pencil contains lead. Is the statement correct? If not, correct it.

(h) The melting point of diamond is very high. Explain the reason.

11 Write notes on (a) Graphite, (b) Adsorption, (c) Activated charcoal, (d) Ivory black, (e) Phosphorus etc. (f) Bleaching action of chlorine. Give three processes.

12 Complete the equations



13 A is a colourless solid melting at 44°C . When heated with caustic soda solution it yields a gas which is spontaneously inflammable in air. If A is exposed to sunlight it slowly becomes scarlet red, but the change may be hastened considerably by heating the solid in absence of air to about 260°C . Identify the solid 'A'.

14. A black powder when heated with NaCl and conc. H_2SO_4 gives off a greenish yellow gas. The gas on (a) passing through liquor ammonia liberates N_2 , (f) on passing through boiling KOH yields compounds one of which when heated with the black powder evolves O_2 . Name the gas and the black powder. Explain the chemical reactions involved with equations.

CHAPTER 4 : Oxides of non-metals.

1. Describe with a neat diagram, the laboratory method of preparation of carbon monoxide. How is it collected? Compare the properties of carbon monoxide with those of carbon dioxide. Why is it dangerous to burn coal in a very limited supply of air?

2. State with equations what happens when carbon monoxide reacts with the following substances :

(a) chlorine, (b) caustic soda, (c) nickel powder, (d) ammoniacal cuprous chloride. State two important uses of carbon monoxide.

3. How is carbon dioxide prepared in the laboratory? How does it react with the following substances?

(a) Lime water, (b) Ammonia, (c) Burning magnesium, (d) Burning potassium. State some of the uses of carbon dioxide.

4. How is carbon dioxide converted into carbon monoxide and vice versa? Describe experiments to prove that both gases contain carbon. What is meant by dry ice?

5. Answer the following questions correctly :

(a) Why is not dil. sulphuric acid used in the preparation of carbon dioxide in the laboratory?

(b) Name one reagent that can be used at room temperature, to distinguish between the two in each of the following pairs.

(i) Nitric oxide and nitrous oxide. (ii) Sulphur dioxide and carbon dioxide.

(c) State the reasons why SO_2 has both oxidising and reducing properties.

(d) How will you free traces of (i) sulphur dioxide from carbon dioxide, (ii) carbon monoxide from carbon dioxide, (iii) nitric oxide from nitrous oxide?

(e) How will you identify carbon dioxide and carbon monoxide?

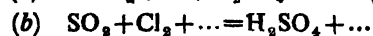
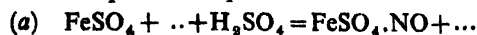
(f) You are given two jars of colourless gases containing hydrogen and carbon monoxide. How will you identify each by a single experiment?

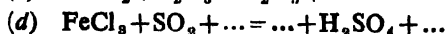
(g) Give reason why carbon dioxide cannot be used for extinguishing fires caused by the burning of metallic magnesium.

6. Write notes on : (a) Dry ice, (b) Silica gel, (c) Fire-extinguisher.

Why is an ordinary soda-acid type of fire extinguisher incapable of extinguishing magnesium-fire?

7. Complete the equations :





8. State with equations what happens when :

(a) Chlorine is passed through a mixture of red hot silica and coke, (b) Sulphur dioxide is passed through a solution of potassium dichromate acidified with dilute sulphuric acid, (c) Sulphur dioxide is passed through an acidified solution of potassium permanganate, (d) Carbon dioxide is continuously passed through lime water and the products are boiled.

9. How does silica occur in nature ? How is pure silica prepared ? Under what conditions does it react with (a) Carbon (b) NaOH. (c) HF ? State the equations.

Mention some of the uses of silica. Compare the properties of silica and carbon dioxide.

10. Write down the names of the five oxides of nitrogen. Give a brief comparative account of the properties of these oxides. Why is nitrogen tri-oxide called a mixed anhydride ?

11. Describe briefly (with sketches) the laboratory methods of preparation of nitrous oxide and nitric oxide. State some of the important physical and chemical properties of these oxides. Write down the equations of principal reactions taken place in the ring est.

12. Name two important oxides of phosphorus. How would you prepare them ? Discuss the action of water on each of them.

13. How will you prepare sulphur dioxide in the laboratory starting from sulphuric acid. Explain, with equations, the reaction of sulphur dioxide with the following :

(a) Aqueous solution of chlorine, (b) Lime water, (c) Ferric chloride solution, (d) Hydrogen sulphide, (e) Sodium hydroxide solution

How will you prove that sulphur dioxide contains sulphur ?

14. Illustrate experimentally four important chemical properties of sulphur dioxide. How is sulphur dioxide converted into sulphur trioxide ? Comment on the bleaching action of sulphur dioxide.

15. A sodium salt (A) on heating gave a solid (B) and oxygen. B on treatment with dilute acid evolved a brown gas. B on heating with NH_4Cl gave a colourless gas and a solid residue C. A on heating with NH_4Cl evolved a colourless gas and a residue same as C. Identify A, B and C and write equations for the reactions.



16. A mixture of three gases A, B and C are passed first into an acidified dichromate solution when A is absorbed turning the solution green. The remainder of the gas is passed through an excess of lime water which turns milky, resulting in the absorption

of B. The residual gas C is absorbed by an alkaline pyrogallol solution. However, the original gaseous mixture does not turn the lead acetate paper black. Identify A, B and C.

[A = SO_2 ; B = CO_2 ; C = O_2]

17. A white powder A when heated gives off a gas which turns lime water milky but does not turn the paper soaked in acidified potassium dichromate solution green. The solid residue left is slightly soluble in water giving an alkaline solution. Identify A.

CHAPTER 5 :

Oxy acids

1. How is nitrous acid prepared ? State some reactions with equations to indicate that it acts as an oxidising agent. How are nitrous acid and a nitrite detected ?

Explain why nitric acid has oxidising property only but nitrous acid has both oxidising and reducing properties.

2. How is nitric acid prepared in the laboratory ? Give a short account of the chemical properties of the acid. How does the acid react with (a) Cu (b) Zn (c) Mg. State reason of the following :

Iron dissolves in dilute nitric acid but not in concentrated nitric acid.

What is aqua regia ? How can you account for its strong oxidising property ?

3. Discuss, with equations, the action of nitric acid on the following non-metals and the compound :

(a) Carbon (b) Iodine (c) Phosphorus (d) Ferrous sulphate solution acidified with dil. sulphuric acid

4. How can phosphoric acid be obtained from bone ash ? Discuss the action of heat on this acid. Give a brief account of the properties of phosphorus acid and phosphoric acid.

5. How would you prepare an aqueous solution of sulphurous acid ? Discuss its acid and reducing properties with suitable examples. How is a sulphite detected ?

6. Describe, in brief, the laboratory method of preparation of sulphuric acid. Write down the equations of the reactions involved in the process. State some of the important uses of the acid.

Prove experimentally that (a) sulphuric acid is a dibasic acid, (b) it is a strong oxidising agent (c) it is a dehydrating agent and (d) it is less volatile than HCl and HNO_3 .

Name two gases which are dried by concentrated sulphuric acid and name three gases which cannot be dried by conc. H_2SO_4 .

7. State with equations, the action of sulphuric acid on (a) sulphur (b) carbon (c) copper (d) lead (e) potassium nitrate (f) barium nitrate. How is sulphate radical detected ?

8. Sulphuric acid acts as an acid, an oxidising or as a dehydrating agent. In which way does it react when it acts on (i) Sugar (ii) Sulphur (iii) Calcium carbonate (iv) Copper ?

9. Describe experiments in brief to show that,

- (a) sulphuric acid contains oxygen, sulphur and hydrogen
- (b) nitric acid contains hydrogen and oxygen
- (c) phosphoric acid contains phosphorus.

10. State the reasons (with equations) why

(a) hydrochloric acid instead of sulphuric acid is not used in the preparation of nitric acid (b) conc. sulphuric acid is not used for drying ammonia, hydrogen sulphide and hydrogen iodide (c) iron and zinc standing over hydrogen in the electro-chemical series are unable to liberate hydrogen from dilute nitric acid. (d) dil. nitric acid is not used in the preparation of hydrogen sulphide from ferrous sulphide (e) Starch solution turns blue when added to a solution of potassium nitrite and potassium iodide acidified with dilute sulphuric acid. (f) Aluminium containers can be used for storing concentrated nitric acid.

CHAPTER 6 : Hydrides of non-metals

1. How is ammonia prepared in the laboratory ? Give a sketch of the apparatus used. Comment on the method of drying of gas. State the principal properties and uses of ammonia.

Describe experiments to show that (i) ammonia is highly soluble in water and the aqueous solution is alkaline (ii) ammonia is a reducing agent at high temperature (iii) ammonia contains hydrogen and nitrogen.

2. How and under what conditions does ammonia react with the following substances ?

(i) Metallic sodium (ii) Cupric oxide (iii) Lead monoxide (iv) Carbon dioxide (v) Oxygen (vi) Copper sulphate solution (vii) Ferric chloride solution (viii) Silver nitrate solution (ix) Silver chloride suspended in water.

What happens when the product obtained by the action of ammonia on sodium is treated with water ? Explain the above reactions with equations.

3. How would you prepare and collect phosphine in the laboratory ? What is a vortex ring ? Describe with equations the action of phosphine on (a) chlorine, (b) copper sulphate solution, (c) silver nitrate solution, (d) hydrogen iodide. Compare the properties of phosphine with those of ammonia.

4. Describe the laboratory method of preparation of hydrogen sulphide. Draw a neat sketch of the Kipp's apparatus and explain how it is used for the preparation of sulphuretted hydrogen. Name

any two other gases which can be prepared readily with the help of the apparatus. Name the chemicals required for the generation of the two gases and give the equations of the reactions.

5. Explain the uses of hydrogen sulphide in the analysis of inorganic salts.

6. Give a brief account of the laboratory method of preparation of hydrogen chloride. How is its aqueous solution prepared? State the important properties and uses of the compound.

7. Describe with neat diagrams the methods of preparation of hydrogen bromide and hydrogen iodide in the laboratory. Explain why these substances cannot be prepared by the same method used in the preparation of hydrogen chloride.

8. Give a comparative account of the properties of hydrochloric, hydrobromic and hydroiodic acids.

(a) State the chemical reaction by which potassium bromide and potassium iodide can be distinguished.

(b) Show with suitable reactions which of the two acids HBr and HI is more easily oxidised.

9. State giving equations and mentioning the visible change, if any, what happens when :

(a) Silver nitrate solution is added to a solution of sodium chloride and the product is first treated with excess of ammonium hydroxide and then with nitric acid.

(b) The product obtained on addition of lead nitrate solution to a solution of sodium iodide is boiled and then cooled subsequently.

(c) Hydroiodic acid is added to an acidified solution of potassium permanganate.

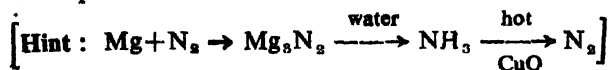
(d) Conc. hydrochloric acid is dropped on potassium permanganate.

(e) The gaseous product obtained by boiling white phosphorus with caustic soda solution is passed through copper sulphate solution.

(f) A solution of sodium nitrate is heated with zinc dust and caustic soda.

10. How would you prove that (a) ammonia is a compound of nitrogen and hydrogen (b) hydrogen sulphide contains hydrogen and sulphur (c) ammonia possesses reducing property?

11. A gas is passed over heated magnesium. The product is treated with water and a new gas obtained. When this gas is passed over heated copper oxide, the original gas is recovered. What is the gas? Explain the reactions.



12. A sodium salt 'A' is treated with NH_4Cl solution and heated when N_2O is produced. The same compound 'A' on strong heating gives 'B' and O_2 . Compound 'B' on heating with NH_4Cl solution gives N_2 . Again, the compound 'A' when boiled with Zn dust and NaOH solution, produces a gas 'C' which gives a brown precipitate with $\text{K}_2[\text{HgI}_4]$ solution containing 'KOH'. Identify A, B, C.

13. A gaseous hydride when brought in contact with hydrogen chloride produces dense white fumes. The hydride gives a deep blue coloration when passed in excess into a copper sulphate solution and is absorbed by fused calcium chloride. Write down the reactions and identify the hydride.

CHAPTER 7 : Manufacture of some important Chemicals

1. Give a short account of the manufacture of ammonia by Haber's process. Explain the theoretical principles involved. State with equation what happens when ammonia and carbon dioxide are passed into water containing suspended calcium sulphate.

2. Discuss the method of preparation of nitric acid on a large scale from ammonia by oxidation. State the conditions necessary for this oxidation. Why are ammonia and oxygen not kept in contact with the catalyst for a long time?

3. (a) How are nitrogen and hydrogen required for the preparation of ammonia by Haber's process obtained?

(b) What should be the volumetric composition or the volumetric proportion of the two gases nitrogen and hydrogen?

(c) Why is the gas-mixture of nitrogen and hydrogen subjected to high pressure?

(d) The gaseous reaction, though reversible and exothermic is not carried out at a low temperature. Why?

(e) Name the catalyst used in the process.

(f) What would be the effect of increasing nitrogen concentration on the equilibrium concentration of ammonia?

(g) How is the ammonia produced separated from the unreacted gas-mixture? What is done with the residual unreacted gas mixture?

4. How are urea and ammonium sulphate manufactured starting from ammonia? Name a phosphatic fertiliser you have read and discuss its preparation on a large scale.

5. Give a short account of the methods of industrial preparation of nitric acid starting from (a) atmospheric oxygen and nitrogen and (b) Chille saltpetre.

6. Give a brief account of the manufacture of sulphuric acid by the contact process explaining clearly the physico-

chemical principles involved. Give a sketch of the commercial plant used.

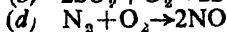
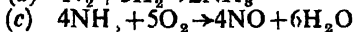
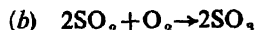
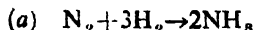
7. How will you convert—

(a) Nitrogen into ammonia and vice versa.

(b) Sulphur dioxide into sulphur trioxide and vice versa

(c) Ammonia into nitric acid and vice versa ?

8. State the suitable conditions under which the following reactions are made to occur.



9. What is coal gas ? Name the main constituents of it. How is coal gas manufactured ? What are the important byproducts of coal gas industry and state their uses.

10. Write notes on : (a) Super phosphate of lime (b) Spent oxide (c) Urea (d) Oleum (e) Sulphan.

West Bengal Higher Secondary Examination

CHEMISTRY (First Paper)

Group A

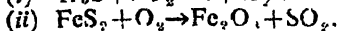
Answer Questions 1 and any three from the rest.

1. 'C' is a compound. 30 gms. of it on analysis give, 10 gms. of an element 'A' and 20 gms. of another element 'B'. If 15 gms. of A and 50 gms. of B are mixed and reacted what weight of C will be produced and what will be the total weight of the mixed substances ?

Or, The density of a gaseous element is 5 times that of oxygen under similar conditions. If the molecule of the element is triatomic, what will be its atomic weight ?

2. (a) Explain 'oxidation number'. What do you understand by "Reduction" ? How are these two related ?

(b) Complete the following equations with the help of 'oxidation number' :



3. (a) What amounts of Na_2CO_3 will be required to prepare the following solutions ?

- (i) 250 c.c. 0.5N Na_2CO_3 (ii) 500 c.c. 0.5M Na_2CO_3
(iii) 1000 c.c. 5% Na_2CO_3 (Na=23)

(b) 25 c.c. of a 0.1N NaOH solution neutralise 22.5 c.c. of a HCl solution. How much water is to be added to 500 c.c. of the HCl solution to make it 0.1N ?

4. (a) State Avogadro's hypothesis. How many molecules are there in 9 gms water and in 18 gms steam ?

(b) Prove that—(i) The mol. weight of a gas is twice its vapour density. (ii) One mole of a gas occupies 22.4 litres at N.T.P.

5. (a) 100 c.c. oxygen and 100 c.c. nitrogen each collected at 25°C and 760 mm pressure are mixed in a vessel of vol 100 c.c. The temperature is maintained at 25°C. What will be the pressure of the gas mixture ? State the related law. What is partial pressure of a gas ? Explain the law related to partial pressure.

(b) What is the difference between the two equations $PV = RT$ and $pv = nRT$?

6. (a) Why will there be difference in the results if CaCO_3 is heated in the open and in a closed vessel ? (b) Explain with illustrations the importance of Dulong and Petits' law. (c) What is equivalent weight of an element ? Explain the relation of equivalent weight and valency.

Group—B

Answer Question 7 and any three from the rest.

7. (a) How and why does nitrogen obtained from air differ from nitrogen obtained from NH_4NO_3 ?

(b) Explain with equations how permanent hardness of water is removed by the Clarke's process.

8. (a) How is sulphuric acid made by the contact process ?

(b) Show with suitable examples how conc. H_2SO_4 and dil. H_2SO_4 differ in properties.

(c) How can H_2SO_3 (sulphurous acid) be prepared from sulphuric acid ?

9. (a) How can ozone be obtained from oxygen ? Prove that ozone and oxygen are primarily the same element.

(b) How does ozone react with the following :

(i) Powdered silver ; (ii) KI solution ; (iii) H_2O_2 solution.

10. State facts in support of the following (any four) :

(i) Hydrogen can be prepared from acid, water and alkali.

(ii) A catalyst increases the rate of reaction. (iii) HI acid is a reducing agent. (iv) SiO_2 is an acidic oxide. (v) Red phosphorus is chemically less active than white phosphorus.

11. (a) Give the methods of preparation and uses of the following : (i) Superphosphate of lime ; (ii) Coal gas.

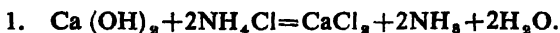
(b) Why is coal gas poisonous ?

12. State with equation what happens when :

(i) Steam is passed over red hot iron. (ii) Steam is passed over strongly heated coke. (iii) A mixture of conc. HNO_3 and P_4O_{10} is warmed. (iv) PH_3 gas is led into CuSO_4 solution. (v) Bromine is dropped into a mixture of red phosphorus and water.

Group 'A'

Answer Question 1 and any Three from the rest.



Find from the above equation the amount in grams of NH_4Cl required to produce 2.024 litres of NH_3 at 750 mm. pressure and Also, find the weight of CaCl_2 produced. ($\text{Ca}=40$)

OR

0.6 gm. of a metal on reacting with acid produces 500 c.c. Hydrogen at N.T.P. and 0.12 gms of the metal produces 0.20 gm of Oxide when burnt. Again 0.56 gm of Oxygen produces 0.63 gm of water. Show that the above facts can be explained with the help of one law of chemical combination. State the law.

2. (a) How will you identify whether a solution is acidic, alkaline or neutral ?

(b) One gram of CaCO_3 is heated to produce lime. The lime produced is dissolved in 1 litre of water. Calculate the normality of the solution.

(c) 50 c.c. 0.8% NaOH solution is mixed with 25 c.c. of 0.5 NaHCl solution. What will be the acidic or alkaline normality of the mixed solution ?

3. (a) When Zinc is added to a solution of a lead compound Zn goes into solution and Pb comes of the solution but nothing happens when lead is added to a solution containing Zinc—Why ?

(b) Of the two processes used in the laboratory for making hydrogen and H_2S gases which is of oxidation-reduction type and why ?

(c) Explain with suitable illustrations that with change in oxidation number of an element its equivalent weight also changes.

(d) Complete the following equation with the help of oxidation number.



4. (a) 1.986 gms of Copper gives 2.470 gms CuO . If 0.346 gm. of Zinc be added to a copper sulphate solution it replaces 0.335 gm Copper from solution. What is the equivalent weight of Zinc ?

(b) Which one is more heavy—1 gram mole of NO or 0.5 gram mole of NO_2 ? Calculate the number of Nitrogen atoms in each. Calculate the mass of one atom of Nitrogen. (N—14, O—16).

5. (a) In the Haber process of industrial production of ammonia the following equation is used :

$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 + 11.8 \text{ Kilo Calories heat.}$ Stating the concerned law explain the effect of change in temperature and pressure on the reaction.

(b) Why the above reaction is carried out at 550°C ?

(c) Will the reaction lead to completion if it is carried in a closed vessel ? What will be the effect of continuous removal of ammonia produced ?

6. Write notes on :

- (i) Avogadro's number (ii) Gas constant 'R' (iii) Hydrolysis (iv) Diffusion of gases.

Group 'B'

Answer question No 7 and any *three* from the rest.

7. State with equations how Chlorine and Oxygen react with Phosphine and Ammonia.

OR

Show with suitable reactions which of the two acids HBr and HI is more easily oxidised

8. Describe with equations how starting with nitrogen and hydrogen urea can be made. What happens when urea is slowly heated ?

9. State with equations what happens when : (any four)

- (i) Slaked lime is mixed with permanent hard water.
- (ii) Red phosphorus is boiled with conc. HNO_3 .
- (iii) Conc. HCl is added to KMnO_4 crystals.
- (iv) Chlorine is passed into hot conc. NaOH solution.
- (v) A solution of SO_2 is mixed with a solution of K_2CrO_4 .
- (vi) A mixture of sand and Na_2CO_3 is fused by heating.

10. (i) Why conc. H_2SO_4 is not used in preparation of H_2O_2 ?

(ii) For the preparation of H_2O_2 , BaO_2 is made into a paste with water—Why ?

(iii) Prove with suitable illustrations that H_2O_2 is a powerful oxidising agent.

(iv) How does H_2O_2 react with an acidified solution of KMnO_4 ? Show that this reaction is of oxidation reduction type.

11. (a) Give a brief account of CO as a fuel and as a reducing agent.

(b) How can sulphurous acid solution and dilute sulphuric acid be identified ?

(c) State why dilute sulphuric acid is not used in making CO_2 from marble stone.

Why lime water turns turbid in contact with CO_2 ?

(d) Name two chemical compounds which can absorb CO and CO_2 gases.

12. State reasons in favour of the following statements (any four) :

- (i) Neutral NO becomes acidic in contact with Oxygen
 - (ii) H_2S is a reducing gas
 - (iii) Charcoal and diamond are different forms of the same element.
 - (iv) Chlorine and Iodine are elements of the same class.
 - (v) Water is the main source for industrial hydrogen.
- — — —

CHEMISTRY—First paper

Group—A

Answer question 1 and any three from the rest.

1. (a) Equal masses of two gases *A* and *B* are kept in two separate vessels at the same temperature and pressure. If the ratio of the molecular weights of *A* and *B* is 2 : 3, find the ratio of the volumes of the two vessels.

(b) What volume of carbon dioxide gas at standard temperature and pressure may be obtained from one kilogram of calcium carbonate ? [$\text{Ca} = 40$]

Or, (a) 1 litre of a gaseous element reacts with 2 litres of another gaseous element to form 1 litre of a gaseous compound (all the volumes being measured at the same temperature and pressure). Both the elements are known to be diatomic. Taking the symbols for the two element as *X* and *Y* respectively, find the molecular formula of the compound.

(b) If the volume per gram of a gas be 280 millilitres at the standard temperature and pressure, what is its molecular weight ?

2. Explain what is meant by the 'partial pressure' of a gas, and state Dalton's law of partial pressures.

A mixture containing 2.0 gm hydrogen and 8.0 gm oxygen is kept at 27°C in a vessel whose volume is 20.0 litres. What is the total pressure inside the vessel ?

3. (a) State Dulong and Petit's law.

(b) 1.020 gm of a metallic oxide contains 0.540 gm of the metal. Calculate the equivalent weight of the metal, and hence its atomic weight with the help of Dulong and Petit's law. Taking

the symbol for the metal as M , find the molecular formula of the oxide. [Specific heat of the metal is 0.216 calorie per degree per gram].

4. (a) Explain the difference between 'normal' and 'standard' solutions of an acid.

(b) If 40.0 millilitres of a sulphuric acid solution be required for titrating 2.65 gm of sodium carbonate dissolved in water using methyl orange as the indicator, what is the normality of the acid ? [$\text{Na} = 23$].

Explain whether there would have been any difference, if phenolphthalein, instead of methyl orange, were used as the indicator.

5. (a) Explain the electronic concept of oxidation and reduction with suitable examples, and show that oxidation and reduction with suitable examples, and show that oxidation and reduction occur simultaneously.

(b) Explain with suitable examples that the oxidation number of the same element may be positive in one of its compounds and negative in another.

(c) Complete the following equation with the help of oxidation number :



6. Explain what is meant by the state of equilibrium of a chemical reaction.

Write the expression for the equilibrium constant for the under-mentioned reaction $2M(\text{gas}) + N(\text{gas}) \rightleftharpoons 2P(\text{gas})$

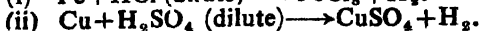
Suppose that the above reaction is endothermic, and that at a definite temperature and pressure M , N and P are in equilibrium in a closed vessel. Now, (i) if the volume of the vessel be increased, keeping the temperature unchanged will the amount of P increase or decrease ? (ii) If the temperature be increased, keeping the volume unchanged, will the amount of P increase or decrease ?

Give reasons for your answer in each case.

Group—B

Answer question 7 and any three from the rest

7. State with reasons whether you expect the reactions to occur as shown below :



+ heat



Or, (a) State with reasons whether concentrated sulphuric acid and quicklime are suitable or unsuitable for drying hydrogen iodide and ammonia.

(b) Name any two good drying agents other than the two mentioned above.

8. (a) Under what conditions does water react with (i) iron and (ii) coke, and what are the products? Give equations.

(b) Explain whether a dilute aqueous solution of magnesium sulphate will behave as 'hard water'.

9. (a) Explain, with a sketch, how Kipp's apparatus can be used for a ready supply of hydrogen sulphide whenever required in the laboratory.

(b) State and explain what happens when hydrogen sulphide is passed into a solution containing both CuCl_2 and ZnCl_2 , acidified with dilute hydrochloric acid.

10. (a) What is 'superphosphate of lime'? How is it prepared?

(b) State with equations what happens when :—

(i) White phosphorus is heated with a concentrated solution of potassium hydroxide. (ii) Water is slowly added to a mixture of red phosphorus and iodine.

(c) How can white phosphorus be converted into red phosphorus?

11. (a) Explain the following phenomena :—

(i) Most chlorine is a strong bleaching agent, but it cannot bleach the marking made with an ordinary pencil; (ii) Iodine is sparingly soluble in water, but its solubility is much higher in a solution of potassium iodide.

(b) State with equations how you will prepare :

(i) nitric acid from ammonia and (ii) ammonia from nitric acid.

12. State with equations what happens when (any four) :—

(i) Ozone is allowed to react with ethylene. (ii) A mixture of gaseous carbon dioxide and ammonia is heated under high pressure. (iii) A burning magnesium wire is inserted into a jar of carbon dioxide. (iv) A mixture of ammonium chloride and sodium nitrite solutions is heated. (v) Nitrogen gas is passed over heated metallic calcium.

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Group—A

1. (a) Is the number of molecules in mole of a gas at 100°C and 300 mm pressure equal to, greater than or less than Avogadro number?

(b) A mixture of hydrogen and oxygen contains 20% by weight of hydrogen. What is the total number of molecules present per gram of the mixture?

Or, (a) Two metals *A* and *B* have the same equivalent weight. but the atomic weight of *B* is twice that of *A*. How can it be explained ?

(b) If the equivalent weight of a metal (*M*) be *x*, and the formula of its oxide be M_mO_n , show that the atomic weight of

$$M = \frac{2xn}{m}$$

2. State the law of 'reciprocal proportions' for chemical combination.

A, *B* and *C* are three elements. 1g *A* combines with 1.33g *B*; 1g *B* combines with 0.125g *C*; 1g *C* combines with 6.00g *A*. Show whether these results are in agreement with the law of reciprocal proportions.

Explain this law with the help of atomic theory.

3. (a) What is meant by 'vapour density'? Establish the relation between vapour density and molecular weight.

(b) What is 'empirical formula'? How can the molecular formula of a gaseous compound be obtained from its empirical formula ?

(c) 60 ml of a mixture of CO and H_2 was mixed with 40 ml oxygen and exploded in a eudiometer. After cooling, the volume was found to be 30 ml. Find the composition of the original mixture. [Volumes were measured at the same pressure and temperature].

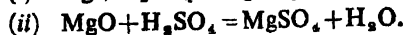
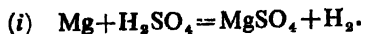
4. (a) Find the value of the 'gas constant' *R* in any unit. (b) Find the volume of 2?g carbon dioxide at 27°C and 570 mm pressure. (c) State Graham's law of diffusion with one example.

5. (a) Explain with one example what is meant by an amphoteric oxide.

(b) Explain why an aqueous solution of ammonium chloride is acidic.

(c) 100 ml of a solution of calcium hydroxide required 20 ml of a 0.030 N HCl solution for neutralisation. Find the normality of the alkali solution. How many grams of calcium hydroxide present per litre of this solution ? [*Ca* = 40]

6. (a) Explain whether the two reactions, stated below, are oxidation reduction reactions :



(b) Explain the significance of the relative positions of hydrogen, iron and copper in the electropotential series. (c) Write the expression for the equilibrium constant (*K*) for the reaction.

